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Oxidative Degradation of Organic Acids Conjugated with Sulfite Oxidation in Flue Gas Desulfurization

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Degradation	Adipic Acid		14G	
Sulfites	Carbon Dioxide		07B	
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ABSTRACT

Organic acid degradation conjugated with sulfite oxidation has been studied under flue gas desulfurization (FGD) conditions. The oxidative degradation constant, k_{12}, is defined as the ratio of organic acid degradation rate and sulfite oxidation rate times the ratio of the concentrations of dissolved S(IV) and organic acid. It is not significantly affected by pH or dissolved oxygen in the absence of manganese or iron. However, k_{12} is increased by certain transition metals such as Fe, Co, and Ni and is decreased by Mn and halides. Lower dissolved S(IV) magnifies these effects. A free radical mechanism was proposed to describe the kinetics. Hydroxy and sulfonated carboxylic acids degrade approximately three times slower than saturated dicarboxylic acids; while maleic acid, an unsaturated dicarboxylic acid, degraded an order of magnitude faster. A wide spectrum of degradation products of adipic acid were found, including carbon dioxide - the major product, smaller dicarboxylic acids, monocarboxylic acids, other carbonyl compounds, and hydrocarbons.

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PROJECT SUMMARY

S.1 INTRODUCTION

Currently, limestone scrubbing is the dominant commercial technology for flue gas desulfurization (FGD) (Laseke et al., 1984). The performance of limestone scrubbing is chemically limited by two pH extremes: (a) low pH near the gas/liquid interface which decreases the solubility and absorption rate of SO_2; and (b) high pH near the liquid/solid interface which decreases the solubility and dissolution rate of limestone (Rochelle and King, 1977; Chang and Mobley, 1981). Organic acids that buffer between pH 3.0 and pH 5.5 enhance SO_2 removal efficiency and limestone utilization at concentrations of 5 to 10 mM (Rochelle and King, 1977; Rochelle, 1982; Rochelle et al., 1984; Chang and Mobley, 1981).

Adipic acid was the first organic acid buffer additive successfully and generally applied to FGD processes up to commercial scale (Chang and Mobley, 1981; Rochelle, 1982; Borgwardt, 1979; Head et al., 1979). It has been replaced commercially by waste dibasic acid (DBA), a waste from adipic acid and cyclohexanone production, containing primarily adipic, glutaric, and succinic acids. DBA was found to be as effective as adipic acid (Chang and Mobley, 1981; Rochelle, 1982). Other potential alternatives include hydroxycarboxylic acids and sulfonated carboxylic acids (Rochelle et al., 1984; Chang, 1979; Weems, 1981). They are of interest because of reduced volatility and potentially lower degradation rates.

In addition to the expected loss of organic acid additive by entrainment of solution in waste solids, loss by chemical degradation (Meserole et al., 1979) and coprecipitation (Jarvis et al., 1982) is also observed. Chemical degradation, which is conjugated with sulfite oxidation (Meserole et al., 1979), is the most important mechanism of buffer loss under forced oxidation conditions (Chang and Mobley, 1981; Rochelle, 1982)

Assuming that both oxidation and degradation are free radical reactions proceeding by a common radical, previous investigators proposed a simple kinetic model (Meserole et al., 1979) which can be expressed as:

$$d[A]/dt - k_{12}([A]/[S(IV)]_d(d[S(IV)]_t/dt) \qquad (S.1)$$

where [A] and [S(IV)] represent organic acid and sulfite/bisulfite molar concentrations, respectively, and the subscripts 'd' and 't' denote 'dissolved' and 'total' respectively. The most probable free radical here is SO_4^- because of its reactivity toward alcohols which are inhibitors of sulfite oxidation (Hayon et al., 1972). It has also been cited as the active species in the decarboxylation/oxidation of organic acids by peroxydisulfate ($S_2O_8^{2-}$) (Vasudeva and Wasif, 1972; Norman et al., 1970).

Valeric acid, glutaric acid, and hydrocarbons from ethane to butane have been identified as degradation products of adipic acid (Meserole et al., 1979; Jarvis et al., 1982). Low pH, especially in the presence of manganese, reduced the degradation rate of adipic acid (Rochelle et al., 1982; Hsiang, 1981). It was also observed that high dissolved S(IV) reduced the degradation rate (Chang, 1982).

It is desirable to understand the degradation kinetics, the mechanism, and the additional environmental impact caused by degradation. This work covers the degradation kinetics, mechanism, and products. Since decarboxylation is the major degradation pathway and since it is decarboxylation that significantly affects the buffering capacity, CO_2 evolution rate instead of the actual degradation rate is of greater interest. The oxidative degradation constant, k_{12}, will be used for most kinetic studies, since this constant is simply the degradation rate normalized with the oxidation rate and the concentrations of organic acid and dissolved S(IV).

S.2 EXPERIMENTAL APPARATUS AND PROCEDURE

Since organic acid degradation is conjugated with sulfite oxidation, an experimental design is required that permits measuring the rates of organic acid degradation and sulfite oxidation simultaneously. Two approaches are used for this study. One oxidizes calcium sulfite slurry; the other, sodium sulfite solution. The slurry system has a large capacity of sulfite to allow significant degradation of organic acid with relatively low $[S(IV)]_d$, typical of actual scrubber conditions. The solution system provides better control of dissolved S(IV). Two reactors have been used to study organic acid degradation during sulfite oxidation. One is an open semibatch reactor while the other is a closed system, semibatch reactor which enables monitoring the gas phase degradation products, primarily carbon dioxide. Figure S.1 gives the block diagram of the experimental apparatus with the closed system reactor.

In a typical slurry experiment, 1.0 M synthesized $CaSO_3$ solids (Hsiang, 1981) were slurried and oxidized in a solution containing 10 mM organic acid and 0.1 M $CaSO_4.2H_2O$ seed crystals. All experiments were performed at a constant temperature of 55°C. The pH was maintained constant throughout a given experiment. In a typical sodium sulfite solution experiment, ~1 mM dissolved S(IV) was maintained constant by titrating with sodium sulfite solution during the oxidation of S(IV) to S(VI). 0.3 M sodium sulfate was added to prevent dramatic change in the ionic strength. The oxidation rate of S(IV) was reflected by the titration rate of sodium sulfite solution.

Total S(IV) was analyzed by iodimetric titration of the slurry sample. Filtered samples were reheated to 55°C, the experimental temperature, and the pH was adjusted back to the original pH (4.50 - 5.50 ±0.01) with sodium sulfite or air oxidation. Then iodimetric titration was used to measure the dissolved S(IV). Carbon dioxide was monitored continuously by an infrared CO_2 detector. Hydrocarbons, organic acids and liquid phase degradation products

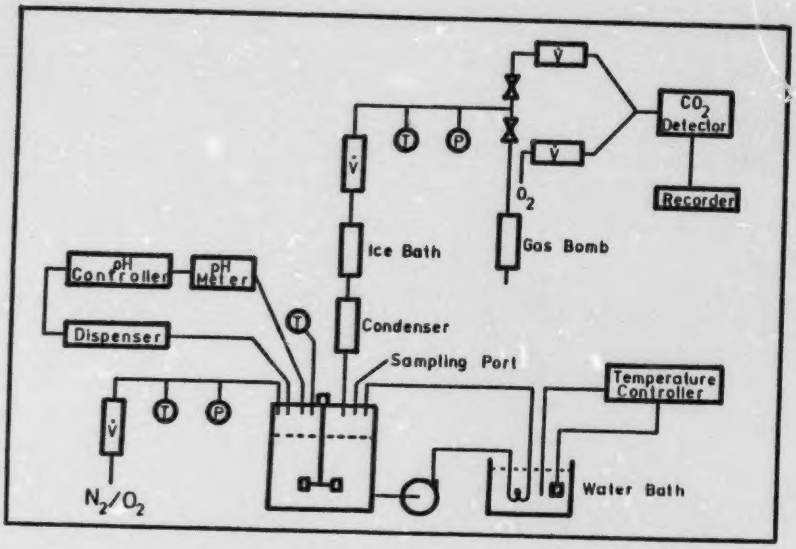
V̇
CO$_2$ Detector
T
P
V̇
V̇
Recorder
O$_2$
Gas Bomb
Ice Bath
pH Controller
pH Meter
T
Condenser
Dispenser
Sampling Port
Temperature Controller
V̇
T
P
N$_2$/O$_2$
Water Bath

Figure S.1: Closed System Apparatus

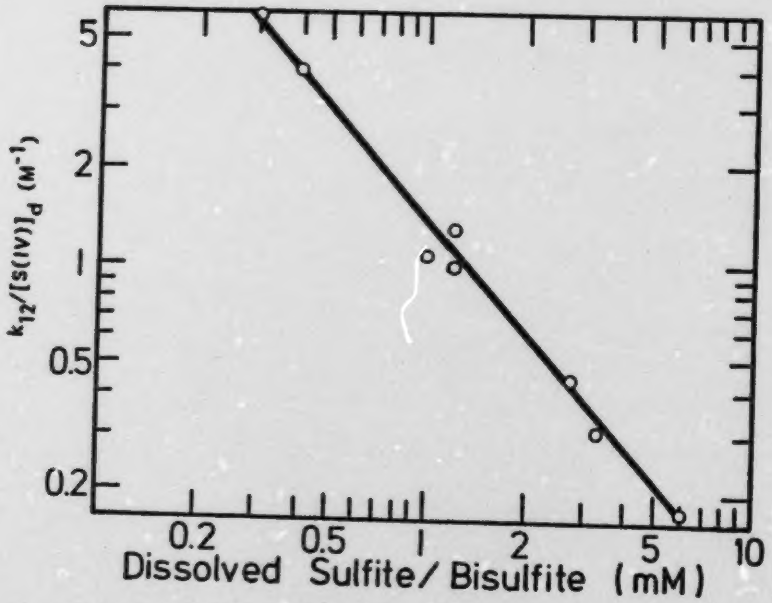

Figure S.2: Effect of Dissolved S(IV) on the Degradation of Glutaric Acids: sodium sulfite solution, closed reactor, 55°C, pH 5

were analyzed by ion chromatograph exclusion (ICE, Dionex 14), gas chromatograph (GC, Varian 3700), and/or gas chromatograph - mass spectrometer (GC/MS, Finnigan 4023). More detailed procedures and conditions are available elsewhere (Rochelle et al., 1984).

S.3 KINETICS

Most of the experiments were performed with adipic acid or glutaric acid. Adipic acid is effective, nonvolatile, and has been extensively tested up to commercial scale. Glutaric acid is the major component of waste dibasic acid (DBA) from adipic acid production. The kinetic results presented below are applied to adipic and glutaric acids only, unless specified.

S.3.1 CONJUGATION WITH SULFITE OXIDATION

No degradation of organic acid was detected when sulfite oxidation is inhibited by adding inhibitors such as sodium thiosulfate and hydroxyl compounds and by depleting oxygen or S(IV) species. When the oxidation rate controlled by the sodium sulfite feedrate increases from 0.0082 to 0.024 M/hr, the oxidative degradation constant, k_{12}, only changes from 1.17×10^{-3} to 0.99×10^{-3}. In slurry experiments, the sulfite oxidation rate is around 1 M/hr, about 100 times greater than the aforementioned rates. An oxidative degradation constant, k_{12}, of 2×10^{-3} could be obtained with the introduction of the estimated dissolved S(IV). The higher value of k_{12} for the slurry system is probably due to the addition of iron to the system through the dissolution of calcium sulfite and calcium sulfate solids. Therefore, the organic acid degradation rate is directly proportional to the sulfite oxidation rate.

S.3.2 pH AND DISSOLVED S(IV)

A number of slurry experiments suggest that the degradation rate increases with increasing pH (Hsiang, 1981). However, dissolved S(IV) is significantly affected by pH in the slurry system (Table S.1). Experiments with

Table S.1 Steady State Solution Composition in CaSO3 Slurry as a Function of pH, Closed Reactor, 55°C, no Organic Acid

pH —	Fe* (mM)	Mn** (mM)	$[S(IV)]_d$ (mM)	Sulfite Oxidation Rate_(M/hr)
4.0	0.15	0.43	34.2	0
4.0	0.13	0.43	27.0	0.5
4.5	0.12	0.45	24.8	0
4.5	0.12	0.46	14.5	0.5
5.0	0.02	0.46	9.3	0
5.0	0.02	0.46	5.9	0.5
5.5	<0.01	0.47	3.9	0
5.5	<0.01	0.46	1.3	0.5

* 0.1 mM was added
** 0.5 mM was added

Table S.2 Effects of Transition Metals on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Conc (mM)	Oxidative Degradation Constant, $k_{12} \times 10^3$					
	Co	Ni	Cu	Ti	V	Cr
0	0.81	0.89	0.87	0.86	1.10	0.99
0.03	0.84	-	0.89	-	-	-
0.1	0.76	1.18	0.93	-	1.23	1.03
0.3	0.82	-	1.00	0.90	1.43	1.02
1.0	0.99	2.48	1.31	0.86	1.46	1.02
3.0	1.60	-	1.33	0.84	1.54	-
10.0	3.30	-	-	-	-	-
oxidation state	2,3	2,3	1,2	3,4	2,3,4,5	2,3,6

the sodium sulfite solution system without manganese or iron at pH 5.0 suggest that the apparent effect of pH on k_{12} in the slurry system is due to the variation of dissolved S(IV) as pH changes (Figure S.2). In addition to affecting dissolved S(IV) in the slurry system, pH also affects the distribution of sulfite and bisulfite and the degree of protonation or dissociation of organic acid, which might be important in the degradation kinetics. Further studies showed no effect of pH on k_{12} when the dissolved S(IV) was kept ~1 mM for three different catalyst environments (Figure S.3). Figure S.3 also shows that in the presence of 0.1 mM Fe k_{12} decreases as the pH increases over 5.0.

S.3.3 TRANSITION METALS

It was shown in Figure S.3 that k_{12} is increased by iron and decreased by manganese. Sodium sulfite solution experiments show that it is the ratio $[Fe]/[S(IV)]_d$ (Figure S.4) or $[Mn]/[S(IV)]_d$ (Figure S.5) that controls k_{12}. In Figure S.4, a background level of 0.0007 mM iron is assumed acording to the correlation result which will be discussed later. The decrease of k_{12} with increasing pH in the presence of 0.1 mM iron (Figure S.3) may be due to decreasing solubility of iron at higher pH.

The first series of transition metals (except Sc and Zn) were studied in sodium sulfite solution. Among these, Co, Ni, and probably Cu appear to increase the oxidative degradation constant, k_{12}, while Ti, V, and Cr are inert (Table S.2). Thallium showed a minor inhibiting effect on the degradation of organic acid in the slurry system. The effect of thallium was not detectable in the sodium sulfite solution system, probably because of interference with the measurement of dissolved S(IV).

S.3.4 HALIDES

It has been reported that the decomposition of carboxylate salts during sulfite oxidation is suppressed by the presence of 0.5 to 3 M chloride in the aqueous absorbent. Table S.3 lists the resulting k_{12} values of adipic

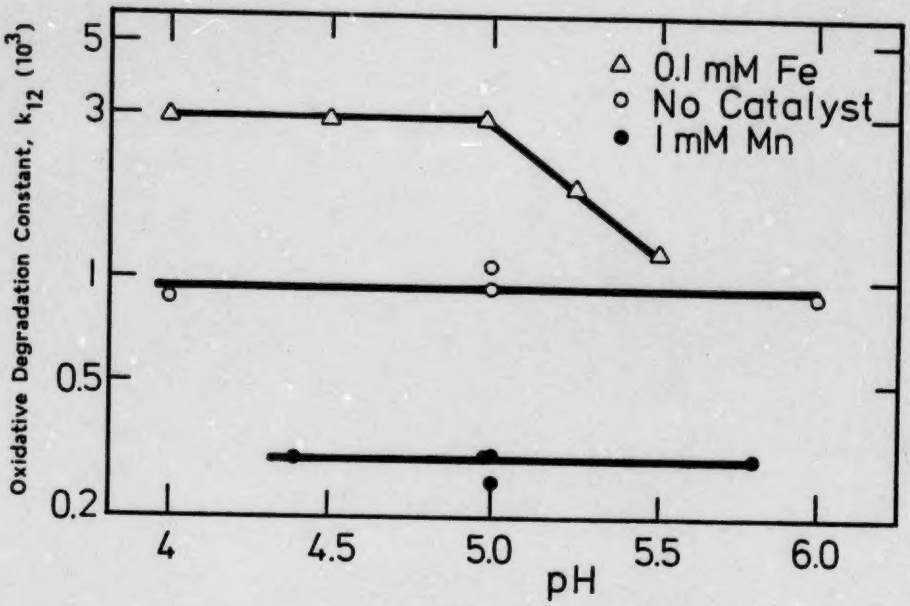

Figure S.3: Effect of pH on the Degradation of Glutaric Acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1 mM

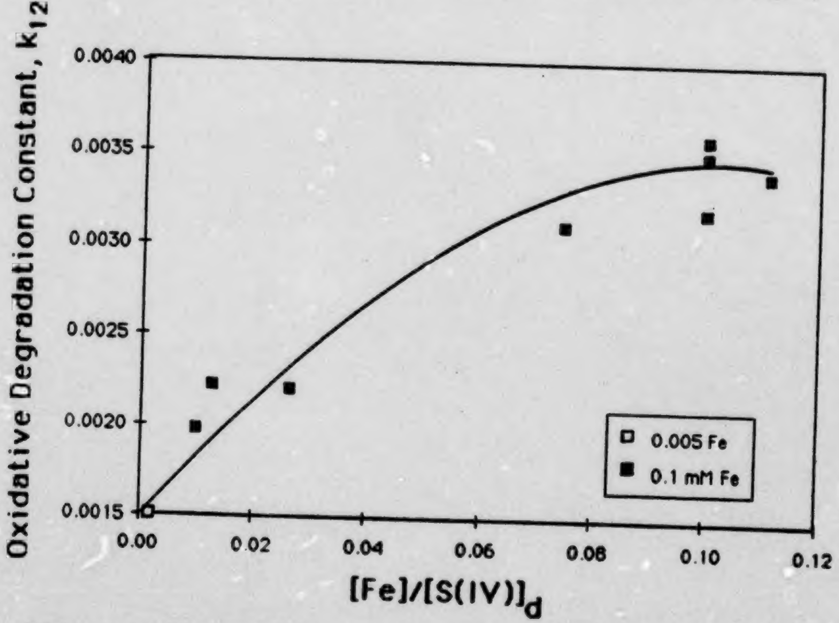

Figure S.4: Effect of Fe on the Degradation of Adipic Acid (Sodium Sulfite Solution): closed reactor, 55°C

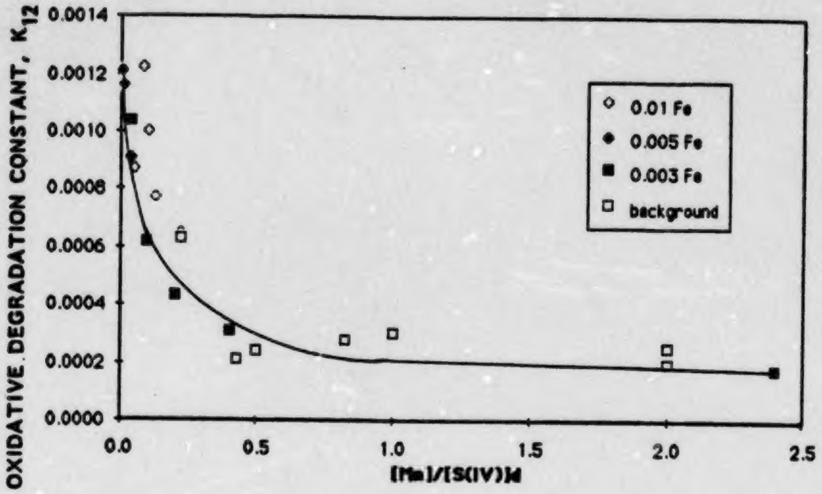

Figure S.5: Effect of Mn on the Degradation of Adipic Acid (Sodium Sulfite Solution): closed reactor, 55°C, pH 5

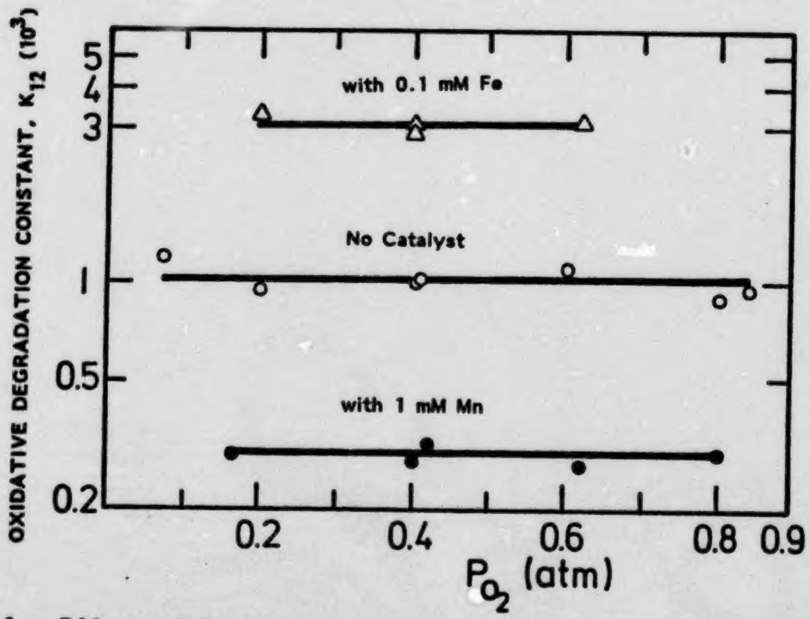

Figure S.6: Effect of Oxygen on the Degradation of Glutaric Acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1 mM

Table S.3 Effects of Halides on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Oxidative Degradation Rate Constant, $k_{12} \times 10^3$

Conc.(mM)	KCl	KBr*	KI*	$MnSO_4$
0	1.0	2.7	3.1	1.0
0.1	-	2.3	0.1	0.7
0.3	-	2.0		0.3
1	-	1.5		0.3
10	-	0.2		
30	0.8			
100	0.6			
300	0.3			

* with 1.0 mM Fe

Table S.4 Comparison of Organic Acids Buffer Additives in terms of k_{12} at pH 5.0, 55°C, in Sodium Sulfite Solution by CO_2 Evolution

Organic Acid	Oxidative Degradation Rate Constant, $k_{12} \times 10^3$			
	$[S(IV)]_d$ (mM)	1 mM Mn	No Catalyst	0.1 mM Fe
Adipic	1.0	0.3	1.0	3.0
Glutaric	1.0	0.3	1.0	3.0
4-Hydroxybutyric	1.0	0.1	---	1.4
Hydroxyacetic	1.0	0.2	---	1.0
Malic	6.0	---	---	1.4
3-Hydroxybenzoic	2.0	0.3	---	-
2-Hydroxybenzoic	3.0	0.4	---	-
Benzoic	1.5	0.8	---	---
Sulfosuccinic	1.5	0.1	0.3	0.3
Maleic	5.0	3.6	6.7	7.0

acid with different concentrations of chloride, bromide, and iodide. Manganese effects are included for the convenience of comparison. In sodium sulfite solution, chloride reduces k_{12} significantly only when its concentration is as high as 100 mM. On the other hand, the iodide effect is so strong that even in the presence of 0.1 mM Fe, 0.1 mM iodide reduces k_{12} to 0.1×10^{-3}. The corresponding value for 1 mM Mn in the absence of Fe is approximately 0.4×10^{-3}. The effect of bromide is between that of chloride and iodide. As with manganese and iron, the effect of halides is magnified by low dissolved S(IV) (Table S.3).

S.3.5 THIOSULFATE

Large addition of thiosulfate stops not only sulfite oxidation but also organic acid degradation. When manganese was applied to suppress the inhibiting effects caused by thiosulfate, it was found that in the slurry system at pH 5.5, 1 mM thiosulfate caused reduction of $k_{12}/[S(IV)]_d$ from 0.6 to 0.15 M^{-1}. No significant effects were observed when pH was lower than 5.0. The inhibiting effect of thiosulfate on the degradation of organic acid is probably due to the low dissolved S(IV) at pH 5.5. Being conjugated with sulfite oxidation, the degradation of thiosulfate (Owens, 1984) is faster than that of adipic acid by three orders of magnitude. Reactive free radicals in an environment of low dissolved S(IV) have a significantly higher probability of reacting with thiosulfate rather than organic acid. This effect is not very strong in the presence of high dissolved S(IV) because of the significant reaction of S(IV) with free radicals.

S.3.6 OXYGEN

Figure S.6 shows that there is no effect of oxygen partial pressure on k_{12}, with or without addition of manganese or iron. Therefore, the reaction order of oxygen in degradation and oxidation reactions should be equal and cannot be detected in the oxidative degradation experiments.

S.3.7 ALTERNATIVES

Table S.4 summarizes the oxidative degradation constants of several potential organic acid buffer additives. Maleic acid degrades about seven times faster than saturated dicarboxylic acids, probably due to the presence of conjugated double bonds. In reducing the degradation of maleic acid, Mn is not as effective as in the case of saturated dicarboxylic acids. Fe has little effect on maleic acid degradation. On the other hand, hydroxycarboxylic acids degrade about three times slower than dicarboxylic acids. The smaller oxidative degradation constants of hydroxyacids probably are not due to the formation of an intramolecular hydrogen bond because of the indistinguishable degradation behavior between 3-hydroxybenzoic and 2-hydroxybenzoic acids. Sulfosuccinic acid behaves more or less in the same way as hydroxycarboxylic acids except that Fe has no significant effect on the degradation of sulfosuccinic acid.

S.4 DEGRADATION PRODUCTS

The degradation products of adipic acid are widely distributed. They can be classified as dicarboxylic acids, monocarboxylic acids, hydroxy-carboxylic acids, keto-acids, furans, hydrocarbons, and carbon dioxide (Table S.5). The degradation product distribution is also a strong function of catalyst environment. Carbon dioxide is the primary degradation product for all cases. In the presence of 1 mM Mn, glutaric and valeric acids are major products. In the absence of Mn, glutaric semialdehyde is the major liquid phase product. Although oxygen would be required to generate a smaller dicarboxylic acid, the dissolved oxygen in the presence of 1 mM Mn should be practically zero because of the mass transfer controlled sulfite oxidation. Therefore, Mn may be an effective carrier of oxygen to the degradation product(s).

Table S.5 Degradation Products from 80% Degradation of 10 mM Adipic Acid in Calcium Sulfite Slurry with 0.1 mM Mn at pH 5.0, 55°C in Terms of the Percentage of the Initial Concentration (mM C)

	Di-carboxylic	Mono-carboxylic	Hydroxy-carboxylic	Hydro-carbons	Others
C6	Adipic (20)				Tetrahydro 2,5 furan Dicarboxylic(*)
C5	Glutaric (1.5)	Valeric (0.7)	5-Hydroxyvaleric (2.5)		Glutaric Semialdehyde (6.7) 4-Oxo-pentanoic (0.3)
C4	Succinic (0.1)	Butyric (0.4)	4-Hydroxybutyric (2.5)	Butane (1.0)	Succinic Semialdehyde (*) Furane (0.6)
C3	Malonic (2.3)	--		Propane (*)	
C2		--		Ethane (*)	
C1		Formic (2.0)		Methane (*)	Formaldehyde (*) CO_2(49)

* less than 0.1%

S.5 MECHANISM

Figure S.7 gives a mechanism proposed to rationalize the experimental observations. This mechanism is based on the following assumptions:

(1) Only sulfate radical (eq. S.2) and manganic ion (eq. S.3) react with organic acids to cause significant degradation, primarily decarboxylation.

(2) Other reactions of organic radicals except the degradation of organic acids are negligible.

$$k_{12} = \frac{Kd1}{2ki3}\left(\frac{kp2'}{kp2 + kp2'} + \frac{\dfrac{kp2'}{kp2 + kp2'}}{1 + \dfrac{kp3}{ki1}\,\dfrac{[S(IV)]}{[Fe]}}\right)\frac{\left(1 + \dfrac{kd2}{kd1}\,\dfrac{k14'}{ki2'}\,\dfrac{[Mn]}{[S(IV)]}\right)}{\left(1 + \dfrac{ki4'}{ki3}\,\dfrac{[Mn]}{[S(IV)]} + \dfrac{ki4}{ki3}\,\dfrac{[Fe]}{[S(IV)]}\right)} \qquad (S.16)$$

Recognizing that sulfate radical (eq. S.2) and manganic ion (eq. S.3) react with organic acids at much slower rates than with S(IV) (eq. S.8, S.7) and assuming that intermediates reach steady state concentrations, equation S.1 and the mechanism proposed above lead to an expression of the oxidative degradation constant, k_{12}, (eq. S.16) with three variables: dissolved S(IV), manganese, and iron. Sixty six data points collected from sodium sulfite solution experiments were used for correlation. These data can be grouped as (1) no Mn/no Fe, (2) no Mn/Fe>0, (3) Mn>0/no Fe, and (4) Mn>0/Fe>0. A background concentration of iron (Fe0) is introduced because iron or a comparable catalyst must be present to initiate the reaction. Therefore, equation S.16 ends up with seven adjustable parameters determined by nonlinear regression:

kd1/(2ki3) = 0.0041

kp2'/(kp2 + kp2') = 0.227

kp3/ki1 = 0.0184

(kd2/kd1)(ki4'/ki2') = 0.85

ki4'/ki3 = 11.93

ki4/ki3 = 0.65

$$SO_4^{-} + OA^{-} \xrightarrow{kd1} SO_4^{2-} + OA \qquad (S.2)$$

$$Mn^{3+} + OA^{-} \xrightarrow{kd2} SO_4^{2-} + OA \qquad (S.3)$$

$$OA \xrightarrow{kd0} \text{Degradation} \qquad (S.4)$$

$$Fe^{2+} + HSO_5^{-} \xrightarrow{ki1} Fe^{3+} + SO_4^{-} \qquad (S.5)$$

$$Fe^{3+} + SO_3^{2-} \xrightarrow{ki2} Fe^{2+} + SO_3^{-} \qquad (S.6)$$

$$Mn^{3+} + SO_3^{2+} \xrightarrow{ki2'} Mn^{2+} + SO_3^{-} \qquad (S.7)$$

$$SO_4^{-} + SO_3^{2-} \xrightarrow{ki3} SO_4^{2-} + SO_3^{-} \qquad (S.8)$$

$$SO_4^{-} + Fe^{2+} \xrightarrow{ki4} SO_4^{2-} + Fe^{3+} \qquad (S.9)$$

$$SO_4^{-} + Mn^{2+} \xrightarrow{ki4'} SO_4^{2-} + Mn^{3+} \qquad (S.10)$$

$$SO_3^{-} + O_2 \xrightarrow{kp1} SO_5^{-} \qquad (S.11)$$

$$SO_5^{-} + SO_3^{2-} \xrightarrow{kp2} SO_3^{-} + HSO_5^{-} \qquad (S.12)$$

$$SO_5^{-} + SO_3^{2-} \xrightarrow{kp2'} SO_4^{2-} + SO_4^{-} \qquad (S.13)$$

$$HSO_5^{-} + SO_3^{2-} \xrightarrow{kp3} 2\ SO_4^{2-} \qquad (S.14)$$

$$2\ SO_3^{-} \xrightarrow{kt} \text{stable products} \qquad (S.15)$$

Figure S.7: A Mechanism for the Oxidative Degradation of Organic Acid Conjugated with the Oxidation of S(IV) to S(VI)

[Fe0] = 0.0007 mM

The experimental and calculated values of k_{12} are compared in Figure S.8.

S.5.1 ORGANIC ACID REACTIONS

Peroxydisulfates have been extensively studied for oxidizing organic compounds, especially organic acids (Vasudeva and Wasif, 1972; Vasudeva, 1975). The sulfate radical anion is a well established intermediate in the thermal and photolytical decomposition of peroxydisulfates (Fronaeus and Ostman, 1968; Kolthoff and Miller, 1951; House, 1962) and is believed to be responsible for the degradation of organic compounds (eq. S.2, Norman et al., 1970). Oxidative degradation of organic acids by Mn^{3+} has also been studied (eq. S.3, Anderson and Kochi, 1970).

Additional evidence demonstrates that sulfate radical reacts with organic acid under FGD conditions:

(1) sulfate radical can be easily derived from peroxymonosulfate, SO_5^{-2} , an expected intermediate, by analogy to peroxydisulfate, $S_2O_8^{2-}$.

(2) The ratio of sulfate radical reacting with organic acid to that reacting with S(IV) is consistent between experimental results and literature predictions.

(3) Previous work on oxidative degradation of organic acids by sulfate radical indicates that decarboxylation is the major pathway (Vasudeva, 1975; Shukla, 1976; House, 1961), which is consistent with experimental observations (Table S.5).

The hydroxyl radical is probably not responsible for organic acid degradation at FGD conditions. It is known to react with organic acids and can be generated from sulfate radical by reacting with water or hydroxyl ion. However, reaction of hydroxyl radical with organic acids does not result in simple decarboxylation (Norman et al., 1970) and at pH less than 8.5 the reactions making hydroxyl radicals are negligible.

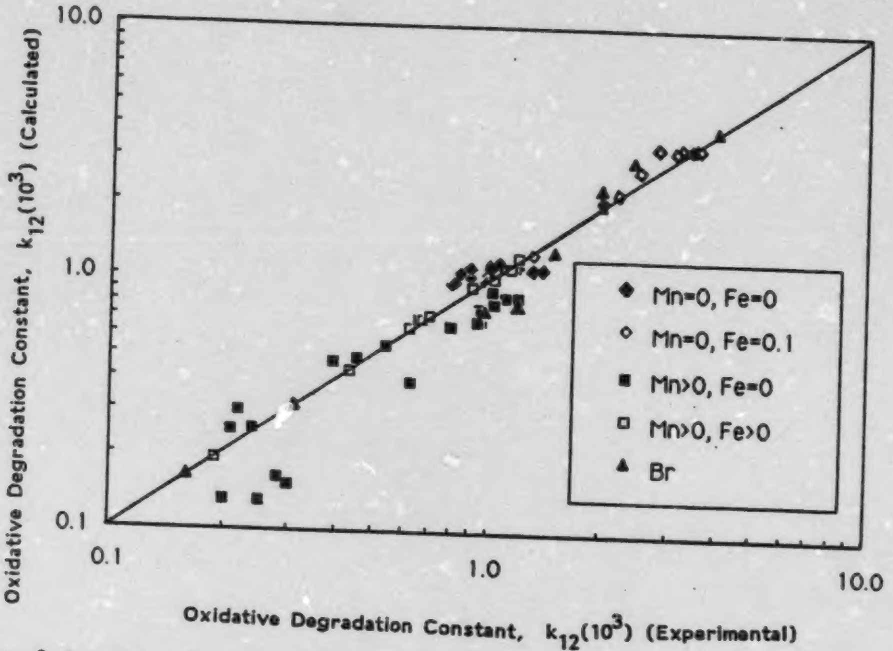

Figure S.8: Comparison of Calculated and Experimental Value of k_{12}

Table S.6 Rates of Sulfate Radical Reactions in Aqueous Solution

Reactant	Estimated $k(M^{-1}S^{-1})$	Literature $k(M^{-1}S^{-1})$	Reference
SO_3^{2-}	-	$\geq 5.3\times10^8$	Hayon et al., 1972
HSO_3^-	-	$>2.5\times5.3\times10^8$	"
Succinate	-	7.1×10^6	Maruthamuthu and Neta (1977)
fumarate	-	1.6×10^7	"
adipate	1.0×10^7	-	-
Fe^{2+}	8.6×10^8	9.9×10^8	Heckel et al., 1966
Mn^{2+}	1.8×10^{10}	-	-
Br^-	1.7×10^9	$(3.5\pm0.4)\times10^9$	Redapath and Willson (1975)
Cl^-		1.3×10^8	Kim and Hamill, 1976
OH^-		4.6×10^7	Roebke et al., 1969
H_2O		10^3-10^4	Pennington and Haim, 1968
HSO_5^-		$<10^5$	Maruthamuthu and Neta, 1977

S.5.2 SULFUR COMPOUNDS REACTIONS

S.5.2.1 Sulfite Radical

The reaction of sulfite radical with O_2 (eq. S.11) provides a way to 'activate' oxygen for the oxidation of S(IV) (Backstrom, 1934; Hayon et al., 1972). The sulfite radical is not very reactive toward organic compounds but reacts at a much higher rate with oxygen and at an even greater rate with itself (Ross and Neta, 1979). The latter reaction is probably the major termination reaction when the reaction rate is controlled by mass transfer of oxygen and is also one of the termination reactions proposed by Backstrom (1934). The stable termination products were reported to be sulfur trioxide and dithionate which will be hydrolyzed to sulfate and sulfite (Ross and Neta, 1979).

S.5.2.2 Sulfate Radical

The sulfate radical is a very reactive one electron transfer oxidizing agent. Some correlated and literature (Ross and Neta, 1979) reaction rate constants are compared in Table S.6. The reaction of sulfate radical with HSO_3^- is believed to be at least 2.5 times faster than with SO_3^{2-} (Ross and Neta, 1979). Therefore, the sulfate radical will react with S(IV) faster at lower pH. In contrast, the sulfate radical reacts with organic acid slower at lower pH (Ross and Neta, 1979). Therefore, a smaller oxidative degradation constant, k_{12}, is expected at lower pH although experimental data do not confirm this projection.

S.5.2.3 Peroxymonosulfate

The peroxymonosulfate radical (SO_5^-) is logically derived from the reaction of sulfite radical with oxygen (eq. S.11). The SO_5^- thus formed reacts with S(IV) to produce sulfate radical(Hayon et al., 1972), sulfite radical, and peroxymonosulfate (HSO_5^-) (Backstrom, 1934) in parallel reactions (eq. S.12, S.13). The coexistence of these two reactions suggests a minimum k_{12} corresponding to the fraction of SO_5^- that reacts with S(IV) to form sulfate radical.

It is suggested (eq. S.16) that the direct production of SO_4^- from SO_5^- (eq. S.13) is not affected by iron while the indirect production of SO_4^- from SO_5^- (eq. S.5) through the formation of SO_5^{2-} intermediate (eq. S.12) is catalyzed by iron. Therefore, SO_5^- is the precursor of SO_4^-, which is the major species responsible for the degradation of organic acid. Since the formation of SO_5^- is inevitable, the degradation of organic acid in conjugation with S(IV) oxidation is also inevitable.

S.5.3 IRON REACTIONS

In the proposed mechanism, free radicals are primarily generated by the reaction between ferrous ion and peroxymonosulfate (eq. S.5). It is well known that ferrous ion reacts with peroxides to form ferric and a free radical formed by splitting the peroxide bond (Kolthoff and Medalia, 1949; Kothoff et al., 1951). Because of the argument made in Section 5.4.2.1, the free radical is thought to be sulfate radical instead of hydroxyl radical. This reaction (eq. S.5) has also been suggested by Huie (1985) and by Rochelle et al. (1985).

Ferrous ion also reacts with sulfate radical (eq. S.9) at a significant rate (Heckel et al., 1966). Therefore, iron generates sulfate radical by reaction with peroxymonosulfate (eq. S.5) but also depletes sulfate radical by direct reaction (eq. S.8). As a result, iron can inhibit or enhance organic acid degradation depending on solution conditions.

S.5.4 MANGANESE REACTIONS

By analogy to the reaction between ferrous ion and sulfate radical (eq. S.9), manganous reacts with sulfate radical (eq. S.10). The latter reaction is necessary for the mechanism to match the observation that manganese decreases k_{12}. The reaction rate constant is estimated to be 1.8×10^{10}. To provide a route for manganous regeneration, manganic ion should also react with S(IV) (eq. S.7) by analogy to the reaction between ferric ion and S(IV) (eq. S.6). The ratio of the reaction rates of Mn^{3+} with organic acid and Mn^{3+} with S(IV), kd2/ki2', was found to be 0.0006, which is an order of magnitude smaller than the sulfate radical counterpart, kd1/ki3 (0.0082).

S.5.5 HALIDE REACTIONS

By analogy to manganese, halides inhibit organic acid degradation by reacting with sulfate radical. The experimental and calculated values of k_{12} with bromide present are compared in Figure S.8.

The correlated value of ki4(Br)/ki3 (1.26) leads to a prediction of 1.7×10^{9} as the reaction rate constant between SO_4^- and Br^-. This constant has been measured as $(3.5\pm0.4)\times10^{9}$ by Redapath and Willson (1975).

Not enough iodide data are available for the prediction of the reaction rate constant between iodide and sulfate radical. However, halides tend to react with organic compounds in the decreasing order: $Cl_2 > Br_2 > I_2$ while halides tend to react with SO_4^- in the increasing order: $Cl^- < Br^- < I^-$ (Ross and Neta, 1979). Therefore, iodide would inhibit organic acid degradation most efficiently while chloride would be the least efficient inhibitor. These trends are expected because of their relative strength in standard electrode potentials.

S.6 CONCLUSIONS

1. The degradation of organic acid is conjugated with sulfite oxidation and can be expressed kinetically in terms of the "oxidative degradation constant", k_{12}, which is defined as:

$$k_{12} = \frac{\text{organic acid degradation rate}}{\text{sulfite oxidation rate}} \times \frac{\text{dissolved S(IV) conc.}}{\text{organic acid conc.}}$$

The oxidative degradation constant, k_{12}, is independent of oxygen mass transfer conditions, organic acid concentration, and pH.

2. The proposed free radical mechanism correlates the experimental k_{12} from 0.0001 to 0.0036 within 30% for 0.3 - 10 mM S(IV), 0 - 0.1 mM Fe, 0 - 1.2 mM Mn, and 0 - 10 mM Br.
3. Sulfate radical is the primary free radical responsible for the oxidative degradation of organic acids.
4. Iron competes with dissolved S(IV) for peroxymonosulfate to produce sulfate radical and hence increases k_{12} from 0.001 to 0.0036 when iron concentration increases from background level (0.0007 mM) to 0.1 mM. No k_{12} over 0.004 has been observed.
5. Manganese competes with dissolved S(IV) for depleting sulfate radical and hence decreases k_{12} from 0.001 to 0.0002 when manganese concentration increases from zero to 1.0 mM. In addition to sulfate radical, manganic ion also causes the degradation of organic acids. Therefore, the effect of manganese is bounded and no k_{12} less than 0.0001 has ever been observed.
6. Halides resemble manganese in reducing k_{12}. With 1 mM dissolved S(IV), 0.1 mM manganese gives effects comparable to <0.1 mM iodide, 1 mM bromide, or 100 mM chloride.
7. Lower dissolved S(IV) magnifies the catalytic and inhibiting effects of iron, manganese, and halides.
8. Thiosulfate inhibits sulfite oxidation and therefore stops organic acid degradation. In the presence of manganese, thiosulfate decreases k_{12} at low levels of dissolved S(IV).

9. Among other transition metals, cobalt and nickel increase k_{12} an order of magnitude less efficiently than iron while thallium appears to reduce k_{12} and titanium, vanadium, chromium and copper have no significant effects.
10. Decarboxylation is the major degradation pathway. In the presence of 0.03 mM manganese, 1.3 mole carbon dioxide is generated from every mole of glutaric acid degradation up to 30% conversion. At high conversion (80%), as much as 49% of the carbon of adipic acid is degraded to carbon dioxide.
11. With 0.1 mM manganese at 80% conversion, The other degradation products of adipic acid are smaller dicarboxylic acids (4%), monocarboxylic acids (3%), hydroxycarboxylic acids (5%), hydrocarbons (1%), glutaric semialdehyde (7%), and other carbonyl compounds (1%).
12. In the presence of high manganese (1.0 mM), the retained degradation products of adipic acid are primarily valeric acid and glutaric acid.
13. Hydroxyacids and sulfonated acids degrade slower than simple dicarboxylic acids by a factor of three while maleic acid, an unsaturated dicarboxylic acid, degrades an order of magnitude faster. Therefore, hydroxyacids and aldehydeacids, which are sulfonated under FGD conditions, tend to accumulate as ultimate liquid phase degradation products.

S.7 RECOMMENDATIONS

1. The oxidation of S(IV) under FGD conditions should be studied further with emphasis on the individual and combined effects of manganese, iron, halides, and free radical scavengers to better understand the mechanism. Dissolved S(IV) and oxygen should be monitored during the experiments to confirm the effects of these two variables.
2. Organic acids and their deliberate derivatives should be studied for oxidative degradation to differentiate electron transfer mechanism and hydrogen abstraction. Decarboxylation and general degradation can then be

discriminated and compared as a function of functional group composition and catalyst environment.

3. The degradation product distribution should be studied as a function of reaction time or conversion to understand better the oxidative degradation of organic acids.
4. The oxidative degradation experiments should be conducted over a broad pH range, 3 to 7, to observe the effect of pH on the degradation of organic acids.
5. Thiosulfate and halides, especially iodide and bromide should be tested in combination with organic acids in FGD scrubbing systems on a pilot plant scale to investigate possible beneficial effects. If oxidation is inhibited, then unsaturated acids such as maleic acid would have makeup rates comparable to DBA or adipic acid.
6. If high level of sulfite oxidation is expected, formic acid and maleic acid are inferior to other alteratives such as DBA and adipic acid.

SECTION 1 INTRODUCTION

The adequate, reliable supply of all forms of energy and the protection of environmental values are two issues of national concern. These concerns are interrelated and each influences the other. The electric power industry of the United States in 1982 generated 73% of the electricity from fossil fuel plants (Melia et al., 1983). It was estimated that about 22.5 teragram of SO_2 was discharged into the U.S. atmosphere in 1981 mostly from coal-fired power plants (EPA, 1982).

Sulfur dioxide is well known to deteriorate the environmental quality affecting plants, animals, and human beings (Houghson, 1966; Wark and Warner, 1981; O'Sullivan, 1985). Several methods and alternatives have been proposed and used for this purpose (Crynes, 1977; Rochelle, 1977):

- change to low sulfur fuels
- use desulfurized coal and oil
- remove sulfur via limestone injection multistage burner (LIMB) process
- remove SO_2 from flue gas
- generate power by nuclear reaction

Among these alternatives, flue gas desulfurization (FGD) is currently favored over the others because of its status of development and cost effectiveness.

1.1 SULFUR DIOXIDE REMOVAL

Flue gas desulfurization processes may be grouped according to: (1) throwaway or salable waste products and (2) wet or dry. Throwaway scrubbing processes remove SO_2 by contact with an alkali solution and dispose of it as calcium sulfite/sulfate solid wastes. Salable scrubbing processes generate elementary sulfur or sulfuric acid as byproducts. The SO_2 removing agents in most throwaway process are not regenerable. As a result, fresh chemicals need to be continually added. Wet or dry processes differ simply by whether or not the end product is wet or dry. A brief comparison of some of the major processes for flue gas desulfurization is listed in Table 1.1.

As indicated in Table 1.2, lime/limestone slurry scrubbing is currently the dominant commercial technology for flue gas desulfurization because of the system simplicity and economics (Smith et al., 1981; Laseke et al., 1984). A simple scrubbing process is schematically presented in Figure 1.1. Flue gas containing 500-5000 ppm SO_2 is contacted with a slurry of product solids at the gas adiabatic saturation temperature, typically 50-55°C. Recycle slurry is given reaction time in the crystallizer to dissolve CaO or $CaCO_3$ and precipitate $CaSO_3$. $CaSO_4$ is also produced to a certain extent because of the presence of oxygen in the flue gas. $CaSO_3/CaSO_4$ waste solids are disposed of after separation from liquid solution which is retained in the system.

One common modification of this process sparges air into the crystallizer to achieve forced oxidation of $CaSO_3$ to $CaSO_4$. $CaSO_4$ solids (gypsum) are easier to dewater and dispose of than $CaSO_3/CaSO_4$ solids (Rossoff, 1974). The dewatering properties of calcium sulfite solids can also be improved by reducing their sulfate content (Rochelle et. al., 1985; Chang and Kaplan, 1983).

1.2 ORGANIC ACID ADDITIVES

Soluble alkali and buffer additives are used to enhance SO_2 removal and/or lime/limestone utilization. Magnesium oxide and organic acids are the most popular additives. Magnesium oxide, usually more attractive for lime scrubbing, basically functions to increase the sulfite alkalinity of the solution. Organic acids, used more frequently in limestone scrubbing, buffer the

Table 1.1 Description of Some Sulfur Dioxide Removal Processes*

PROCESS GENERICS	PROCESS OPERATIONS	ACTIVE MATERIAL	KEY SULFER PRODUCT
A. Throwaway scrubbing processes			
1. Lime or limestone	Slurry scrubbing	CaO, $CaCO_3$	$CaSO_3/CaSO_4$
2. Sodium	Na_2SO_3 solution	Na_2CO_3	Na_2SO_4
3. Double alkali	Na_2SO_3 solution, regenerated by CaO or $CaCO_3$	$CaCO_3/Na_2SO_3$ or CaO/NaOH	$CaSO_3/CaSO_4$
4. Magnesium-promoted lime/limestone	$MgSO_3$ solution, regenerated by CaO or $CaCO_3$	$MgO/MgSO_4$	$CaSO_3/CaSO_4$
B. Regenerative scrubbing processes			
1. Magnesium oxide	$Mg(OH)_2$ slurry	MgO	15% SO_2
2. Sodium	Na_2SO_3 solution	Na_2SO_3	90% SO_2
3. Citrate	Sodium citrate solution	H_2S	Sulfur
4. Ammonia	Ammonia solution, conversion to SO_2	NH_4OH	Sulfur (99.9%)
C. Dry processes			
1. Carbon adsorption	Adsorption at 400°K, reaction with H_2S to S, reaction with H_2 to H_2S	Activated carbon/H_2	Sulfur
2. Spray dryer	Absorption by sodium carbonate or slaked lime solutions	$Na_2CO_3/Ca(OH)_3$	$NaSO_3/Na_2SO_4$ or $CaSO_3/CaSO_4$

* Source: Wark and Warner, 1981.

Table 1.2 Summary of FGD Process Applications

	Operational		Under construction		Contract awarded		Total	
	No.	MW*	No.	MW*	No.	MW*	No.	MW*
Throwaway product								
Wet								
Nonregenerable								
Limestone	51	20,756	13	7,546	11	7,591	75	35,893
Lime	34	13,634	5	3,350	2	1,090	41	18,074
Sodium carbonate	6	1,505	-	-	-	-	6	1,505
Regenerable								
Dual alkali	4	1,572	1	391	1	265	6	2,228
Dry (nonregenerable)								
Lime	5	1,214	7	2,679	4	2,440	16	6,333
Sodium carbonate	1	440	-	-	-	-	1	440
Salable product								
Wet								
Nonregenerable								
Limestone	1	166	1	475	-	-	2	641
Lime	1	65	-	-	-	-	1	65
Regenerable								
Wellman Lord	7	1,959	-	-	-	-	7	1,959
Magnesium oxide	3	724	-	-	-	-	3	724
Dry (regenerable)								
Aqueous carbonate	1	100	-	-	-	-	1	100
TOTAL THROWAWAY PRODUCT	101	39,121	26	13,966	18	11,386	145	64,473
TOTAL SALABLE PRODUCT	13	3,014	1	475	-	-	14	3,489
TOTAL WET	107	40,381	20	11,762	14	8,946	141	61,089
TOTAL DRY	7	1,754	7	2,679	4	2,440	18	6,873
TOTAL NONREGENERABLE	99	37,780	26	14,050	17	11,121	142	62,951
TOTAL REGENERABLE	15	4,355	1	391	1	265	17	5,011

*Equivalent scrubbed capacity

* Source: Laseke et al., 1984

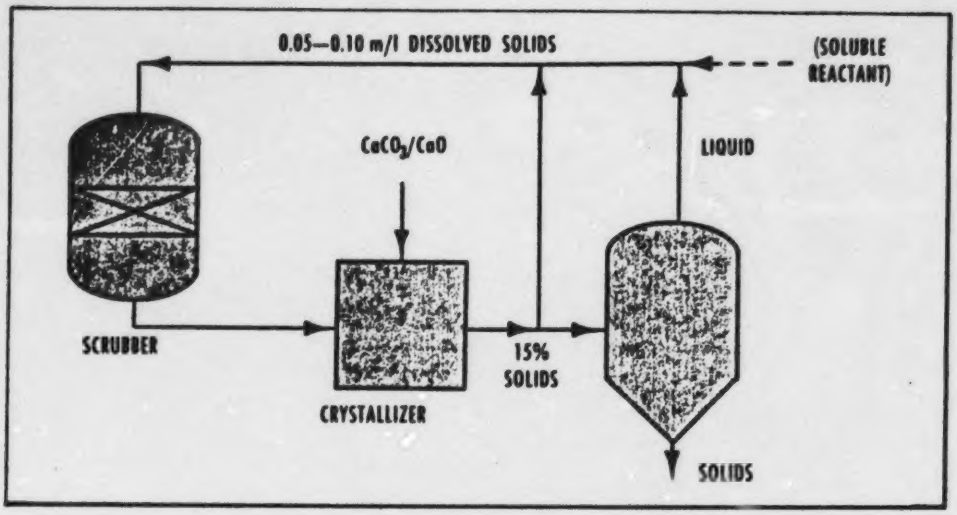
0.05—0.10 m/l DISSOLVED SOLIDS
(SOLUBLE REACTANT)
$CaCO_3$/CaO
LIQUID
SCRUBBER
15% SOLIDS
CRYSTALLIZER
SOLIDS

Figure 1.1: Simple Slurry Scrubbing Process

gas-liquid interface to provide a reasonably high driving force for SO_2 absorption. Organic acids with pK_a values between 3.0 and 5.5 at 5 to 10 mM should be suitable to enhance SO_2 absorption (Rochelle and King, 1977).

In addition to the expected loss of organic acid in the solution entrained with waste solids, organic acid additives are lost by two additional mechanisms: (1) chemical degradation (Meserole et al., 1979); (2) coprecipitation with calcium sulfite/sulfate solids (Terry et al., 1982). The first mechanism is responsible for most of the loss under forced oxidation, while the second one dominates for natural oxidation (Rochelle, 1982; Chang and Mobley, 1981).

1.3 SCOPE

The scope of this work is to characterize organic acid degradation conjugated with sulfite oxidation. The effort will quantify the kinetic variables, develop a model for oxidative degradation, identify degradation products of adipic acid, and explore the degradation of other buffer additives.

Organic acid degradation was studied as a function of sulfite oxidation rate, pH, and the concentrations of organic acid, S(IV), dissolved oxygen, catalysts and inhibitors.

A semibatch reactor was used to measure the rate of sulfite oxidation and organic acid degradation simultaneously. Temperature (55°C) and pH (4.0-6.0) were kept constant. Ion chromatography exclusion (ICE), gas chromatograph (GC), and/or gas chromatograph-mass spectrometer (GC/MS) were used to analyze organic acids and their degradation products. Iodometric titration was used to measure the total and dissolved S(IV) concentration. Offgas was monitored for carbon dioxide to provide the instantaneous degradation rate. The results of these experiments were analyzed to provide information for modeling and provide clues to better understand mechanisms.

SECTION 2 BACKGROUND

2.1 OVERVIEW OF BUFFER ADDITIVES FOR FGD PROCESSES

Lime/limestone slurry scrubbing is the dominant commercial technology for flue gas desulfurization (Rochelle etal, 1984). Lime is produced from limestone by an energy intensive calcination process. The direct use of limestone is becoming more attractive with the rising cost of energy. The performance of wet scrubbers, especially limestone slurry scrubbing, can be limited by reagent reactivity which results in low SO_2 removal efficiency, poor absorbing reagent utilization, and ensuing reliability problems (Chang and Mobley, 1981).

2.1.1 FUNCTION OF ADIPIC ACID

Extensive research has been conducted in the search for mass transfer enhancement additives that improve lime/limestone scrubber performance. Table 2.1 outlines the important milestones in the development and testing of buffer additives (Rochelle, 1982). Unlike other additives such as magnesium oxide which enhance SO_2 absorption by increasing dissolved sulfite alkanility, the function of adipic acid is not adversely affected by forced oxidation (Burbank et al., 1981; Borgwardt, 1979) and high chloride concentration (Borgwardt, 1979). Buffer additives can also be used in lime scrubbing where magnesium oxide is usually more attractive.

Several buffer additives have been proposed for this purpose (Rochelle and King, 1978; Chang, 1979; Chang and Rochelle, 1980; Weems, 1981). Early work by Chemico (Villers-Fisher and Warshaw, 1972) and TVA (Hatfield and Potts, 1972) on acetic and benzoic acids provided the impetus for theoretical analysis of buffer additives by Rochelle (1977), who recommended the use of

Table 2.1 Milestones in Organic Acid Buffer Research

Year	Event	Reference
1969	1% Acetic Acid Enhances SO_2 Removal from 65 to 83% in lab scrubber	Villers-Fisher and Warshaw, 1972
1971	10 mM Benzoic acid enhances SO_2 removal from 50 to 75% in lab scrubber; adipic, glycolic, phthalic acids suggested	Hatfield and Potts, 1972
1973	10 mM Benzoic enhanced SO_2 removal in 2400 acfm pilot plant, turned pond red, 30% of acid unaccounted for	Hollinden et al, 1974
1975	Lab scale tests of adipic, citric, acetic	Wasag et al, 1975
	Mass transfer theory recommends 5 to 10 mM buffer at pK_a 4 to 5, adipic, sulfopropionic, sulfosuccinic recommended	Rochelle and King, 1977
1977	Adipic acid demonstrated in 300 cfm pilot plant with forced oxidation and natural oxidation, valeric acid odor observed	Borgwardt, 1979
1978	Adipic acid demonstrated in 10 MW prototype, material balance suggests unknown losses	Head et al, 1979
1979	Conjugated oxidation identified as loss mechanism, valeric and glutaric found as degradation products	Meserole et al, 1979
	Degradation in 10 MW minimized by low pH	Burbank and Wang, 1981
	Mn identified as degradation inhibitor at low pH	Rochelle et al, 1982a
1981	Coprecipitation identified as additional loss mechanism, Ethane, Propane, butane observed as degradation products	Jarvis et al, 1982
	4-carboxy-butanal identified as a degradation product	Rochelle et al, 1982b
	DBA demonstrated at 300 cfm	Chang and Mobley, 1981
	Adipic and DBA demonstrated at 194 MW	Colley et al, 1982
	Adipic demonstrated in 20 MW industrial	Gerstle et al, 1982
	70-day run in 10 MW, unknown degradation product observed	Wang and Burbank, 1981
1982	DBA demonstrated with 50,000 ppm chloride	Chang and Laslo, 1982
	DBA commercially used at 194 MW	Hicks, 1982

adipic acid. Adipic acid and dibasic acid (DBA) have been tested in pilot-scale, prototype-scale, and full-scale limestone scrubbers and has demonstrated consistent improvement of system performance (Mobley and Chang, 1981; Hargrove, 1980; Garrett, 1984; Burbank et al., 1981; Hicks and Fraley, 1982; Wang and Burbank, 1982; Clarke et al., 1983; Glover et al., 1984; Laslo et al., 1985) Recently DBA has replaced adipic acid because of equivalent performance and lower price (Chang and Mobley 1983; Burnett et al., 1984; Burke et al., 1984; Burke et al., 1985; Guetig et al., 1985).

Scrubber performance is determined by the integrated effect of gas/liquid mass transfer, limestone dissolution, and calcium sulfite dissolution/crystallization. It is limited by two pH extremes: (1) low pH near the gas/liquid interface which decreases the SO_2 solubility and absorption rate; (2) high pH near the liquid/solid interface which decreases the limestone solubility and dissolution rate. A mass transfer theory was developed and recommended that 5 to 10 mM organic acids buffering between pH 3.0 and 5.5 would be enough to maximize the enhancement of SO_2 removal (Rochelle and King, 1977). The mass transfer model simulated the adipic acid function in limestone scrubbing by considering the following reactions:

Sulfur dioxide + Water ---> Acidity + Bisulfite (2.1)

$$[\ SO_2 + H_2O \longrightarrow H^+ + HSO_3^-]$$

Adipate ion + Acidity ---> Adipic acid (2.2)

$$[^-OOC(CH_2)_4COO^- + 2\ H^+ \longrightarrow HOOC(CH_2)_4COOH]$$

Reactions 2.1 and 2.2 show the buffering effect of adipic acid. As adipate ion reacts with the acidity generated by the absorption of SO_2, reaction 2.1 is shifted to the right and SO_2 removal efficiency is enhanced. The model also predicted that SO_2 absorption rate would be higher under forced oxidation conditions due to less interference by the bisulfite ion. These predictions were verified by data from actual scrubbing testing (Borgwardt 1978; Burbank et al., 1981).

Chan and Rochelle (1981) developed a theoretical model to describe the effect of adipic acid on limestone dissolution by the following reactions:

Limestone + Water --> Alkalinity + Calcium ion + Bicarbonate (2.3)

$$[CaCO_3 + H_2O \longrightarrow OH^- + Ca^{2+} + HCO_3^-]$$

Adipic acid + Alkalinity ---> Adipate ion + Water (2.4)

$$[HOOC(CH_2)_4COOH + 2\ OH^- \longrightarrow {}^-OOC(CH_2)_4COO^- + 2\ H_2O]$$

Reactions (2.3) and (2.4) show that the adipate ion consumed by buffering the absorbed SO_2 as shown in reactions (2.1) and (2.2) is replenished as alkalinity generated by limestone dissolution. Laboratory experiments confirmed that the limestone dissolution rate was significantly accelerated by adipic acid (Chan and Rochelle, 1981; Rochelle et al., 1983)

Industrial data (Burke et al., 1985; Glover, et al., 1984; Garrett, 1981; Hargrove, 1980) indicate that the major benefits of organic acid additives include :

- increased SO_2 removal
- decreased limestone consumption
- decreased scaling problem
- decreased waste sludge volume
- reduced operating cost
- expanded FGD system flexibility

2.1.2 BUFFER ALTERNATIVES

Adipic acid is used primarily as a monomer for nylon 66 but is also approved as a food additive. It has two pKa values, 4.4 and 5.4 (Serjeant and

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Dempsey, 1979; Gane and Ingold, 1931). However, accumulation of $CaCl_2$ typically depresses the buffering points to about 4.0 and 5.0 (Cavanaugh, 1978). As a buffer additive in limestone slurry scrubbing, adipic acid is effective, nonvolatile, and has been extensively tested up to commercial scale.

Dibasic acid (DBA) is a waste from adipic acid or cyclohexanone production containing primarily adipic, glutaric, and succinic acids. It is typically half the cost of adipic acid. Four dibasic acids have been tested at the IERL-RTP pilot plant to evaluate and compare the effectiveness of DBA with adipic acid in terms of SO_2 removal efficiency and limestone utilization (Chang and Dempsey, 1983). If "meq./liter" is taken as the basis of organic acid concentration, equivalent scrubber performance can be obtained for DBA and adipic acid. DBA from Du Pont and Monsanto (primarily glutaric acid from adipic acid production) has been successfully tested at the commercial scale, while waste acids from Badishe (primarily adipic acid from cyclohexanone production) have produced some foaming problems in pilot plant testing (Chang and Dempsey, 1982).

Formic and acetic acids are probably volatile under scrubber conditions. However, they may be useful in a two-stage scrubber system with attention paid to recovery of the volatile acids (Chang and Brna, 1986).

Hydroxypropionic and hydroxyacetic (glycolic) acids are sulfite oxidation inhibitors and may be less prone to oxidative degradation. Sulfosuccinic and sulfopropionic acids should give nonvolatile degradation products. Hydroxypropionic, sulfopropionic, and sulfosuccinic acids are not commercially available, but can be easily synthesized by addition of water or sulfite to acrylic acid or maleic anhydride (Smith, 1981). Hydroxyacetic acid is commercially available. It has a lower pKa value (3.85) than the other alternatives and should be relatively more effective in systems at lower pH.

Badishe has another waste acid containing primarily maleic acid that appears to degrade faster than other organic acids (Burke et al., 1984), probably due to the unsaturated double bond. However, in situ or off-site reaction of maleic acid with sulfite to produce sulfosuccinic acid might make this waste acid a suitable buffer additive.

2.1.3 LOSS OF BUFFER ADDITIVES

In addition to the expected loss of organic acid in the solution entrained with waste solids, material balances in pilot plant tests indicated additional loss of adipic acid (Chang and Mobley, 1981). Laboratory research has shown that the unaccounted-for losses are primarily caused by two mechanisms : (1) chemical degradation of adipic acid (Meserole et al., 1979); and (2) precipitation of adipic acid and its degradation products with the calcium sulfite/sulfate solids (Terry et al., 1982). The first mechanism is responsible for most of the loss under forced oxidation conditions, while the second mechanism is more important in the case of natural oxidation (Rochelle, 1982; Chang and Mobley, 1981).

2.1.4 ENVIRONMENTAL IMPACT AND TOXICITY ASSESSMENT

A degradation pathway of adipic acid proposed to cover the potential degradation products is given in Figure 2.1 (Garcia, 1980). These products include monocarboxylic acids, dicarboxylic acids, alkanes, and carbon dioxide. The principle degradation products found have been glutaric acid, valeric acid, and carbon dioxide (Meserole et al., 1979). Alkanes including ethane, propane, and butane have also been identified as degradation products (Jarvis, 1983).

Extensive tests on slurry and sludge from pilot and prototype tests of adipic acid and dibasic acid have shown that the additives introduce no additional problems of sludge toxicity or mutagenicity. Leached toxic elements were all present at levels below those deemed hazardous (Chang and Mobley, 1981, [illegible]). Biological tests including : (1) the mutagenicity

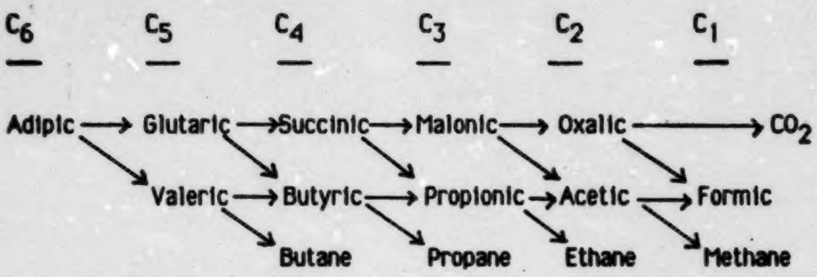
C6
C5
C4
C3
C2
C1
Adipic
Glutaric
Succinic
Malonic
Oxalic
CO2
Valeric
Butyric
Propionic
Acetic
Formic
Butane
Propane
Ethane
Methane

Figure 2.1: Degradation Pathway of Adipic Acid

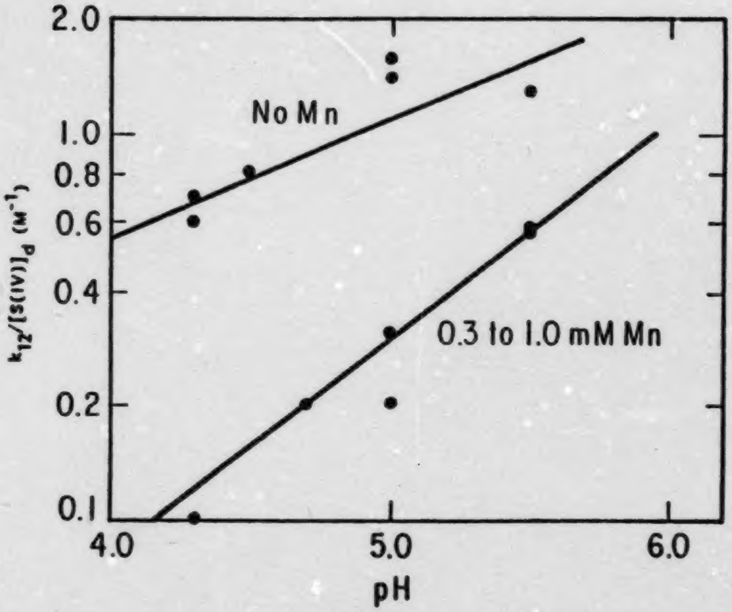

Figure 2.2: Effects of pH and Mn on Organic Acid Degradation: Calcium sulfate slurry at 55°C

assay, (2) CHO clonal toxicity assay, (3) rabbit alveolar macrophage (RAM) cyclotoxicity assay, (4) human cell cytotoxicity assay, (5) rodent toxicity, and (6) fresh water toxicity assay on algae, fish, and invertebrates, have shown no mutagenicity and low or no detectable toxicity.

Organic acid degradation will result in minor additional emission of hydrocarbons and volatile organic acids in the flue gas and oxidizer vent. Chemical analysis of flue gas from the Shawnee venturi/spray tower gave about 2 mg/m^3 more polar organics (probably valeric acid) with adipic acid than the TCA without adipic acid.

Valeric and butyric acids from adipic acid or glutaric acid degradation have a low odor threshold. The odor has been occasionally observed in scrubber tests of adipic acid, but has never required remedial action or avoidance. The odor may be detectable over open tanks, but does not constitute a significant environmental impact (Meserole et al., 1979).

2.2 REVIEW OF OXIDATIVE DEGRADATION

Under typical scrubber conditions, 50-60°C and pH 4-6, the primary mechanism of carboxylic acid degradation is conjugated oxidation (Meserole et al., 1979). Thermal degradation occurs at 270-330°C in aqueous solution or 50-100°C in 1-2 M sulfuric acid solution (Agabekov and Mitskevich, 1967; Kiselva and Dudkin, 1967). Microbial degradation requires microorganisms that are not likely to survive at scrubber conditions (Keith, et. al., 1978; Grulas, 1976).

Degradation of C_2-C_{10} carboxylic acids has been observed in hydrocarbon solution undergoing oxidation (Berezin et al., 1966; Denisov et al., 1977; Tinker, 1970). Three observations support the hypothesis that carboxylic acid degradation is conjugated with free radical oxidation of other chemical species. (1) Degradation of carboxylic acids can be inhibited by free radical scavengers such as phenol and β-naphthol (Agabekov and Mickevich, 1967; Sheldon and Kochi, 1972). (2) Degradation does not take place in the absence of hydrocarbon oxidation (Tinker, 1970). (3) Decarboxylation of carboxylic acids does not occur in the absence of oxygen (Denisov, et. al., 1977).

2.2.1 DEGRADATION KINETICS

A rate expression for adipic acid degradation under scrubber conditions was proposed by previous investigators (Meserole et al., 1979). Assuming that both oxidation (Ulrich, 1983) and organic acid degradation (Denisov et al., 1977) are free radical reactions proceeding by a common free radical, R•

$$d[A]/dt = k_1[A][R\bullet] \tag{2.5}$$

$$d[S(IV)]_t/dt = k_2[S(IV)]_d[R\bullet] \tag{2.6}$$

where [A] and [S(IV)] represent organic acid and sulfite/bisulfite molar concentrations, respectively, and the subscripts 'd' and 't' denote 'dissolved' and 'total' respectively, then the rate of degradation is given by

$$d[A]/dt = k_{12}([A]/[S(IV)]_d)(d[S(IV)]_t/dt) \tag{2.7}$$

where $k_{12} \equiv k_1/k_2$. Previous investigators have correlated rates by k_d defined as $k_{12}/[S(IV)]_d$ (Hsiang, 1981). The constant k_d should only be a function of the variables that affect the solubility of calcium sulfite.

Adipic acid was initially tested as a buffer additive in EPA's pilot plant scrubber at Research Triangle Park (RTP). The scrubber system at RTP consists of a single-loop, 300 cfm spray scrubber and a single hold tank during natural oxidation. Another hold tank was added during forced oxidation. It was an open system, and soluble tracers, Na^- and Cl^-, were added to the slurry to indicate the amount of solution loss. Scrubber solids analysis was neglected at RTP, and rate constants were calculated based on adipic acid losses through degradation and coprecipitation. Most of the experiments were conducted under natural oxidation; therefore, the calculated k_d values are probably on the high side because of significant loss by coprecipitation. k_d

was 0.2-0.9 M^{-1} at pH 4.6 to 6.1. No consistent variation with pH was observed. Several experiments with ferrous iron and flyash showed no effect on degradation (Chang, 1981).

Tests sponsored by EPA at the Shawnee prototype facility were conducted in a variety of 10 MW scrubbers with good material balance, usually closed within 95% (Burbank et al., 1981). The slurry solution normally contained 0.1-1.0 mM manganese accumulated from the flue gas or limestone. Sample solutions were analyzed for adipic acid by the silicic acid titration method, which measures total carboxylic acid concentration. Adipic acid concentration thus determined should be somewhat higher than its actual value.

Radian was contracted by EPA to conduct a systematic study of scrubber operating conditions on adipic acid degradation (Jarvis, 1983; Terry et al., 1982). A bench-scale FGD system capable of closed-loop operation was used to simulate adipic acid degradation in a full-scale FGD system. The significant results are listed below :

- For 0.0323-0.1228 gmole SO_2 absorbed/hr, 9.7-100% oxidation, 6.0-69 mM adipic acid, and pH 4.6-5.5, the degradation rate was correlated by:

  $$R_{d(A)} = 4.1271 \times 10^{-4}[A]^{0.5542}(\%O)^{1.185} \tag{2.8}$$

  where, $R_{d(A)}$, [A], and (%O) are adipic acid degradation rate (mmole adipic/gmole SO_2 removed), adipic acid concentration (mmole), and percent oxidation, respectively.
- With forced oxidation, 0.1 to 0.3 mM Mn causes a significant reduction (42.5-85.4%) in the adipic acid degradation rate; under natural oxidation conditions, Mn has no effect.
- No pH effect was observed in the absence of Mn. In the presence of Mn, a decrease in pH is usually accompanied by a decrease in the adipic acid degradation rate.

- Increasing $[S(IV)]_d$ via the addition of sodium sulfate had no significant effect on k_d.
- The activation energy for adipic acid degradation was 10.6 Kcal/gmole.

Garcia (1980) and Hsiang (1981) studied the oxidative degradation of adipic acid in a batch reactor at The University of Texas. Calcium sulfite slurry was used to provide $[S(IV)]_d$ assuming a saturated solution of calcium sulfite. Their results and some industrial data are summarized in Figure 2.2 which illustrates the effects of pH and Mn.

2.2.2 PROPOSED MECHANISMS

Organic acid degradation is conjugated with sulfite oxidation. In other words, the free radicals generated during sulfite oxidation attack organic acids and cause organic acid degradation. Therefore, the mechanism of sulfite oxidation will be reviewed first.

2.2.2.1 Sulfite Oxidation

Experiments with known free radical scavengers have shown that sulfite oxidation is essentially free radical in nature (Altwicker, 1977). Therefore, the observed kinetics can be expected to follow the form common to this class of mechanism. Noninteger rate order, multi-term expression, variation of kinetic behavior with conditions and general complexity of reaction phenomena are frequently observed.

The oxidation of S(IV) in aqueous solution proceeds according to the following simple stoichiometry :

$$S(IV) + 1/2\ O_2 \ \text{---->}\ S(VI) \qquad (2.9)$$

where S(IV) and S(VI) stand for sulfur compounds with valence states of positive four and six, respectively. Backstrom (1934) proposed that reaction

(2.9) involved a chain mechanism in which a metal ion, M^{n+}, of appropriate oxidation state initiates the radical sequence as follows:

initiation

$$M^{n+} + SO_3^{2-} \longrightarrow M^{(n-1)+} + SO_3^{-} \tag{2.10}$$

propagation

$$SO_3^{-} + O_2 \longrightarrow SO_5^{-} \tag{2.11}$$

$$SO_5^{-} + SO_3^{2-} \longrightarrow SO_5^{2-} + SO_3^{-} \tag{2.12}$$

oxidation

$$SO_5^{2-} + SO_3^{2-} \longrightarrow 2\ SO_4^{2-} \tag{2.13}$$

termination

$$2\ SO_3^{-} \longrightarrow S_2O_6^{2-} \tag{2.14}$$

$$SO_3^{-} + SO_5^{-} \longrightarrow S_2O_6^{2-} + O_2 \tag{2.15}$$

$$2\ SO_5^{-} \longrightarrow S_2O_6^{2-} + 2\ O_2 \tag{2.16}$$

In this mechanism, the initiation step involves a one-electron reducible metal ion as the catalytic initiator. For a truly closed catalytic sequence $M^{(n-1)+}$ must be oxidized back to M^{n+}. The propagation steps involve SO_3^{-}, SO_5^{-}, and SO_5^{-2} as reactive intermediates. The oxidation step is invoked for stoichiometric reasons. The termination steps result in the production of dithionate, a frequently observed but low yield product (Hoffmann and Jacob, 1983).

Hayon et al. (1972) observed the formation of sulfate radical ion, SO_4^{-}, during the flash photolysis and pulse radiolysis of oxygenated sulfite solution. They found alcohols to be effective inhibitors of sulfite oxidation. SO_4^- reacts with alcohols very rapidly while SO_3^- and SO_5^- are relatively inert to alcohols. The mechanism proposed by Hayon et al. is similar in many ways to the Backstrom mechanism with the exception of the inclusion of the sulfate radical ion as a reactive propagation intermediate.

initiation

$$M^{n+} + SO_3^{2-} \qquad M^{(n-1)+} + SO_3^- \qquad (2.17)$$

propagation

$$SO_3^- + O_2 \longrightarrow SO_5^- \qquad (2.18)$$

$$SO_5^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_4^- \qquad (2.19)$$

$$SO_4^- + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^- \qquad (2.20)$$

termination

$$2\,SO_4^- \longrightarrow S_2O_6^{2-} + O_2 \qquad (2.21)$$

$$2\,SO_5^- \longrightarrow S_2O_6^{2-} + 2\,O_2 \qquad (2.22)$$

Several other mechanisms have been proposed to rationalize different investigators' observed kinetics. Different mechanisms result in different rate expressions. The rate expression :

$$-d[S(IV)]/dt = k[M^{n+}]^{\alpha}[S(IV)]^{\beta}[O_2]^{\gamma}[H^+]^{\delta} \qquad (2.23)$$

varies according to different investigators. The ranges are α: 1/2 - 2, β: 0 - 3/2, γ: 0 - 1, and δ: -1 - 1 (Hoffmann and Jacob, 1983).

2.2.2.2 Organic Acid Degradation

The oxidation of organic acid takes place by a free-radical chain mechanism, and is accompanied by decarboxylation (Denisov, et al., 1977).

Carbon dioxide is formed primarily from the carboxylic groups, as established by tracer techniques. In the oxidation of n-butyric and n-valeric acids labeled with ^{14}C in the carboxylic group, the quantity of active CO_2 liberated corresponded to the quantity of acid oxidized to within 2-3% (Denisov et al., 1977). However, in an experiment with adipic acid labeled with ^{14}C in the carboxylic groups, Agabekov and Mitskevich (1968) found that the relative amount of radioactive carbon dioxide did not change with the degree of oxidation and made up almost half (41%) of the total amount of CO_2 formed. Therefore, adipic acid degradation must occur to a certain extent through rupture of the C-C bonds.

The reaction of peroxy radicals with carboxylic groups was suggested to account for CO_2 formation :

$$RO_2\bullet + R_1CH_2COOH \dashrightarrow ROOH + R_1CH_2COO\bullet \qquad (2.24)$$

$$R_1CH_2COO\bullet \dashrightarrow R_1CH_2\bullet + CO_2 \qquad (2.25)$$

This is supported by the study of iosotope effects in the oxidative decarboxylation of R'COOH and R'COOD. When the degradation of trimethylacetic acid is conjugated with the oxidizing of cumene, $k_H/k_D = 6$ at 135°C; $k_H/k_D = 4.2$ (110°C) for acetic acid; and $k_H/k_D = 2.1$ (135°C) for n-butyric acid (Denisov, et al., 1977). However, i-butyric acid decarboxylates under the same conditions without an isotope effect ($k_H/k_D = 1.1$). Therefore, two processes lead to carbon dioxide formation from acids in the oxidation, reaction of the peroxy radical with the carboxylic group and with the methylene group.

It was reported that the nature and rate of the oxidation of acids, other conditions being equal, depended on their molecular weight, and higher acids were readily oxidized by atmospheric oxygen at 115°C while acids with shorter chains ($\leq C_9$) were stable under these conditions. The formation of β-ketoacids in the oxidation of monocarboxylic acids resulted in the conclusion that β-position is the preferential oxidation site. However, the higher activity of the α-CH_2 group is indicated by the data on the reaction of organic acids with free methyl radicals in the liquid phase (Denisov, et al., 1977). According to Price and Morita (1953), the ratio of the rate constants for the removal of hydrogen atom from the α- and β- C-H bonds by methyl radicals (k_α/k_β) is 7.8. The oxidation of propionic, n-butyric, and n-valeric acids chiefly at the α-methylene group has been noted (Denisov, et al., 1977).

In the presence of transition metal salts, the carboxylic group of the acid reacts not only with the peroxy radical but also with the transition metal ion (Stranes, 1966; Clifford and Waters, 1965; Smith and Waters, 1969; Sharau et al., 1969) according to the scheme :

$$\mathrm{RCOOH} + \mathrm{M}^{(n+1)+} \longrightarrow \mathrm{R\text{-}COO\text{-}M}^{n+} + \mathrm{H}^{+} \tag{2.26}$$

$$\mathrm{R\text{-}COO\text{-}M}^{n+} \longrightarrow \mathrm{RCOO}\bullet + \mathrm{M}^{n+} \tag{2.27}$$

$$\mathrm{R\text{-}COO}\bullet \dashrightarrow \mathrm{R}\bullet + \mathrm{CO_2} \tag{2.28}$$

In the oxidation of mixtures of cumene with n-valeric and isobutyric acids, it was observed that the quantity of carbon dioxide liberated, and the induction factor (the ratio of CO_2 generation rate to oxygen consumption rate), increased with increase in the concentration of Co, which influenced not only the oxidation but also the decarboxylation. A possible mechanism has been proposed. The acid, present as a complex with Co, forms a carboxylate radical more readily, leading to an increase in the quantity of CO_2 with increase in the concentration of Co. On the other hand, in the oxidation of azelaic and sebacic acids (150°C) it was established that the addition of cobalt and manganese bromides in quantities greater than 0.06 mole percent decreased the rate of oxidation and decarboxylation, and the induction factor decreased. It can be attributed to chain termination by the reaction of the $RO_2\bullet$ radical with Br^-, with the formation of inactive products.

$$\mathrm{RO_2}\bullet + \mathrm{Br}^- \dashrightarrow \mathrm{HBrO_x} \tag{2.29}$$

where $HBrO_x$ is the oxidized form of bromine, for example, HBrO, $HBrO_2$, etc (Denisov, et al., 1977).

In addition to bromide, other inhibitors (phenols and aromatic amines) were reported to decrease the rate of oxidation by terminating the chain in a reaction with the peroxide radicals (Denisov, et al., 1977; Bamford and Tipper, 1980). It was suggested that for inhibitors capable of forming a hydrogen bond, an inert free radical from inhibitor was formed through proton transfer :

$$RO_2\bullet + HIn \dashrightarrow RO_2\bullet \ldots HIn \dashrightarrow ROOH + In\bullet \qquad (2.30)$$

The active free radical is believed to be SO_4^- under flue gas desulfurization conditions. Hayon et al. (1972) observed that sulfite oxidation was inhibited by alcohols which reacted readily with SO_4^- but not with SO_3^- or SO_5^-. In addition, the SO_4^- free radical generated from the dissociation of $S_2O_8^{2-}$ has been extensively studied in the area of organic acid degradation (Vasudeva and Wasif, 1972; Vasudeva, 1975; Chawla and Fessenden, 1975).

SECTION 3 EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 INTRODUCTION

Since organic acid degradation is coupled with sulfite oxidation, an experimental design is required that permits measuring the rates of organic acid degradation and sulfite oxidation simultaneously. Two approaches are used for this study. One oxidizes calcium sulfite slurry; the other, sodium sulfite clear solution. The slurry method provides sulfite/bisulfite continuously by dissolving calcium sulfite solids. The concentration of dissolved sulfite/bisulfite, $[S(IV)]_d$, is approximately constant at the value fixed by the solubility of calcium sulfite. With clear solution, concentrated sodium sulfite solution is added as necessary to maintain constant pH. $[S(IV)]_d$ is approximately constant and can be fixed from 0.1 to 30 mM. However, sodium sulfate accumulates in solution during the experiment and 0.3 M sodium sulfate is added at the beginning to provide a reasonably constant ionic environment. All chemicals, except calcium sulfite which is synthesized in the lab, are reagent grade.

The slurry system has a large capacity of sulfite to allow significant degradation of organic acid with relatively low $[S(IV)]_d$, typical of actual scrubber conditions. However, it is inconvenient and difficult to control or measure $[S(IV)]_d$. It is much easier to control or measure $[S(IV)]_d$ with clear solution. However, the ionic environment in the clear solution system is different from that in limestone slurry scrubbing. Nevertheless, Ca^{2+}, Na^+, and SO_4^{2+} can be assumed to have little or no significant effect on either sulfite oxidation or organic acid degradation. Whenever only kinetic information is desired, the clear solution system is preferred because of the easy measurement and control of $[S(IV)]_d$, which is a very important variable for the study of organic acid degradation coupled with sulfite oxidation. The slurry method is most useful for studying degradation products.

3.2 PRINCIPLE

3.2.1 CALCIUM SULFITE SLURRY

Typical conditions in the slurry system are:

pH	4.5 - 5.5
Temperature	55°C
Organic acid	10 mM
$CaSO_3.1/2H_2O$ solids	1.0 M
$CaSO_4.2H_2O$ solids	0.1 M

A variable amount of inhibitor (such as thiosulfate) or catalyst (sulfate salt of a transition metal) can be added.

The reactions that occur in the reactor include calcium sulfite hemihydrate dissolution, sulfite oxidation, gypsum crystallization, organic acid degradation, absorption of O_2, desorption of CO_2, and dissolution or precipitation of trace amounts of transition metal ion impurities, especially iron.

Since calcium sulfite solids are usually present in excess, $[S(IV)]_d$ is controlled primarily by the equilibrium:

$$CaSO_3 + H^+ = Ca^{2+} + HSO_3^- \qquad (3.1)$$

The calcium concentration is usually controlled by gypsum solubility. $[S(IV)]_d$ increases when sodium sulfate or magnesium sulfate are added to the solution and it decreases when calcium chloride or calcium nitrate are added. A constant calcium concentration is achieved by starting the slurry experiments with 0.1 M gypsum seed.

The net result of sulfite oxidation in the slurry is dissolution of calcium sulfite and precipitation of calcium sulfate. There is no significant effect of oxidation on pH. However, a slight increase in pH is unavoidable because the primary degradation of organic acid is decarboxylation. Even though the pH change is not as significant as in the absence of pH buffer, the pH change will significantly affect $[S(IV)]_d$. To avoid introducing new species into the reactor, dilute sulfuric acid (5 N) is used to maintain constant pH and therefore to maintain constant $[S(IV)]_d$.

3.2.2 SODIUM SULFITE CLEAR SOLUTION

The conditions for the clear solution system are basically the same as those for the slurry system except that: (1) sodium sulfite is added continuously to maintain constant dissolved S(IV) and pH and (2) 0.3 M sodium sulfate is used to buffer the ionic strength.

The concentration of dissolved sulfite/bisulfite is controlled by the feedrate of concentrated sodium sulfite solution and the agitation rate which affects the sulfite oxidation rate. The addition of concentrated sodium sulfite solution is either fixed at a constant rate or controlled by pH stat to maintain constant pH. The principles can be described chemically in the following equations:

$$HSO_3^- + 1/2\ O_2 \ \text{--->}\ SO_4^{2-} + H^+ \qquad (3.2)$$

$$SO_3^{2-} + H^+ \ \text{--->}\ HSO_3^- \qquad (3.3)$$

Hydrogen ion released from oxidation is neutralized by sodium sulfite with a 1:1 stoichiometric ratio. Therefore, S(IV) and pH remain constant and the oxidation rate can be measured directly from the titration rate of sodium sulfite solution. The same principle has been applied to the study of sulfite oxidation (Ulrich, 1983; Owens, 1984), and calcium sulfite dissolution/crystallization (Tseng, 1984).

3.3 PREPARATION OF CALCIUM SULFITE HEMIHYDRATE SOLIDS

$CaSO_3.1/2H_2O$ is available commercially only in low purity (65%) and contains significant amounts of Fe and Mn (Hsiang, 1981). Therefore the calcium sulfite solids have been synthesized by reaction of calcium chloride and sodium sulfite. 2 M $CaCl_2$ was filtered through Whatman glass microfiber filter paper (934-AH). The pH of 2 M $CaCl_2$ is around 11, high enough to precipitate Fe impurity as $Fe(OH)_3$. The calcium sulfite solids were then prepared by dropwise titration of 1.5 M sodium sulfite into 2 M calcium chloride solution according to the following reaction:

$$Na_2SO_{3(aq)} + CaCl_{2(aq)} = CaSO_{3(s)} + 2\ NaCl_{(aq)} \qquad (3.4)$$

The solids were reslurried with distilled water several times and were rinsed with distilled water several times while filtering through Whatman no.1 filter paper with vacuum. Reslurrying and rinsing were necessary to eliminate NaCl, the major byproduct. A verification of the calcium sulfite purity was later made by iodimetric titration. The major impurity of the synthesized $CaSO_3.1/2H_2O$ was assumed to be calcium sulfate formed by oxidation during preparation.

3.4 APPARATUS

Two reactors have been used to study organic acid degradation during sulfite oxidation. One is an open semibatch reactor (Figure 3.1), while the other is a closed system, semibatch reactor (Figure 3.2), which enables monitoring the gas phase degradation products, primarily CO_2. Figure 3.3 gives the block diagram of the experimental apparatus with the closed system reactor.

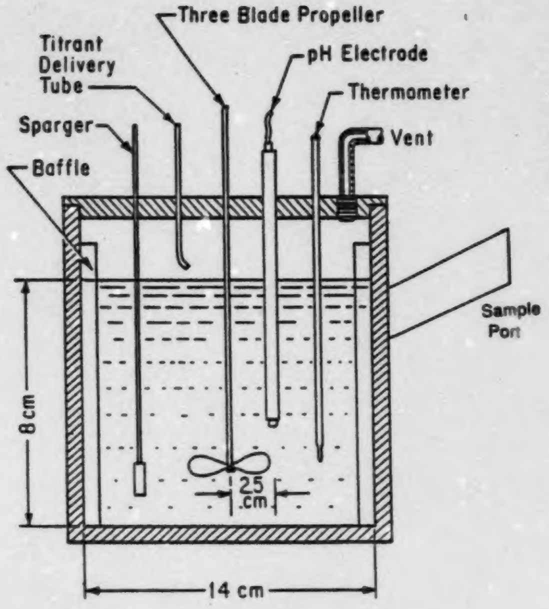
Three Blade Propeller
Titrant Delivery Tube
pH Electrode
Thermometer
Sparger
Vent
Baffle
Sample Port
8cm
25
.cm
14 cm

Figure 3.1: Open Plexiglass Reactor

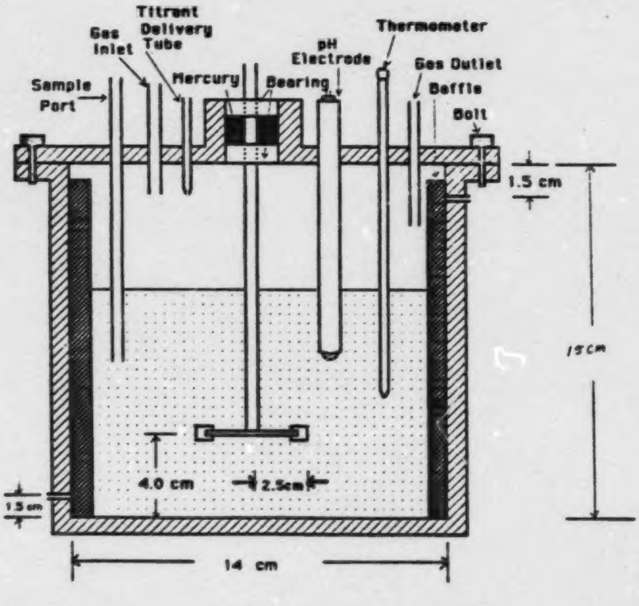
Titrant Delivery Tube
Gas Inlet
Sample Port
Mercury
Bearing
pH Electrode
Thermometer
Gas Outlet
Baffle
Bolt
1.5 cm
15cm
4.0 cm
2.5cm
1.5cm
14 cm

Figure 3.2: Closed Plexiglass Reactor

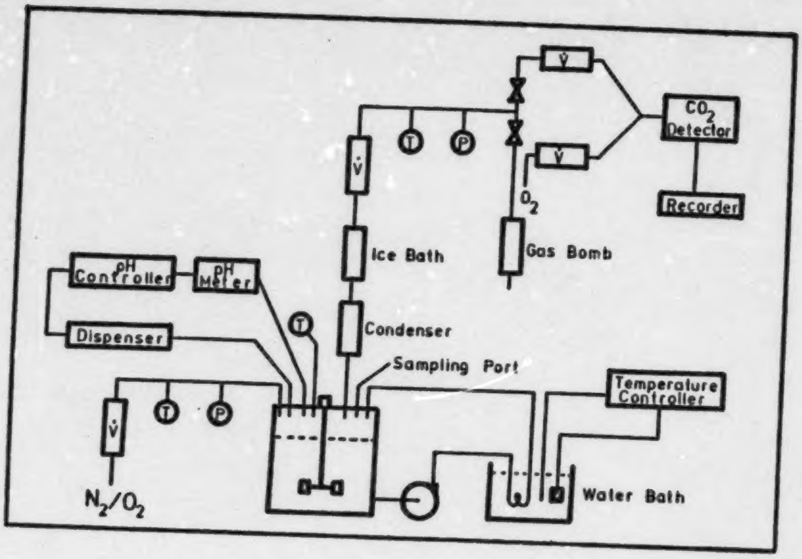
$\dot{V}$
T
P
CO_2 Detector
Recorder
O_2
Gas Bomb
Ice Bath
pH Controller
pH Meter
Dispenser
Condenser
Sampling Port
Temperature Controller
Water Bath
N_2/O_2

Figure 3.3: Closed System Apparatus

3.4.1 OPEN SYSTEM REACTOR

The open system reactor was a plexiglass cylinder, 14 cm in diameter and 14 cm in depth with four baffles preventing vortex formation during solution agitation. The baffles were mounted on the wall of the reactor. The dimensions of the baffles were 0.6 cm in thickness, 1.5 cm in width, and 13.5 cm in length. The same reactor has been used in this lab to study limestone dissolution (Chan, 1981), organic acid degradation (Hsiang, 1981), limestone dissolution - effect of type and grind (Toprac, 1981), sulfite oxidation (Prada, 1982; Ulrich, 1983; Owens, 1984), and dissolution/crystallization of calcium sulfite (Tseng, 1984). One liter of solution was agitated by a three-bladed, 2.5 cm marine propeller which was driven on the fast shaft of a variable speed motor. Agitator speed was measured by counting rotations of a slow shaft directly linked to the agitator, Cole Parmer 4558, with a speed ratio of 1:12.

The pH of the slurry was measured by a Corning combination Ag/AgCl electrode calibrated at 55°C with pH 4 phthalate and pH 7 phosphate buffers. The pH electrode was connected to the Fisher Titrimeter II Titration System, which consisted of a 10 ml burette dispenser, an electrometer, and a titrate demand module. The titrate demand module acted as a remote automatic on/off controller for the burette dispenser. Before the experiment the operating pH was set by the titrate demand module as a titration end point. When a pH increase above the end point was detected, an amount of 5 N sulfuric acid was released by the burette dispenser to neutralize the slurry and restore the initial pH. The acid was added through a slanted glass delivery tube. However, when the pH of the slurry dropped below that of the endpoint, the pH could not be controlled.

The reactor was immersed in a water bath maintained at 55±2°C with a mercury on/off thermoregulator actuating an electric heating coil. The temperature of the reacting slurry solution increased 10 - 20°C during most of the experiments, because of the highly exothermic reaction of sulfite oxidation and the poor conductivity of the plexiglass.

Pure oxygen gas controlled by a rotameter at 100 ml/min was presaturated with water at 55°C before being sparged into the reactor to minimize the concentration change due to water evaporation.

3.4.2 CLOSED SYSTEM REACTOR

The closed system reactor was basically the same as the open system reactor except that the solution was agitated by a blade disk impeller and a bearing sealed with mercury was centered on the lid to make the reactor gas-tight. The impeller was a 3.5 cm diameter disc with six 1.0 cm × 1.4 cm blades. 1.5 liters instead of 1.0 liter of slurry solution was used for the closed system in order to reduce the gas volume and increase the response for CO_2 detection. The temperature of the solution was controlled by circulating the solution through a stainless steel coil immersed in a water bath maintained at 55°C with a proportional electronic temperature controller (Versa-Therm 2156-4). With the aid of the heat exchanger, the reaction solution temperature could be controlled within ±2°C.

Pure oxygen flow rate was measured by a rotameter. It flowed over the head space of the reacting slurry solution instead of sparging into the solution as described in the section of 'Open System Reactor'. The exit gas passed through a spiral condenser chilled with ice water. The moisture in the exit gas is further removed by running through an ice-water bath before entering the CO_2 analyzer, Horiba PIR-2000, with a detection range of 200 ppm to 0.25%. Whenever necessary, the exit gas was diluted with pure oxygen for CO_2 measurement. The oxygen ran through a tube of ascarite II to eliminate contaminated CO_2 and a tube of anhydrous $MgClO_4$ to eliminate moisture before mixing with the exit gas from the reactor to prevent the dissolution of KBr window and the infrared absorption interference caused by water.

3.5 PROCEDURE

3.5.1 SLURRY SYSTEM

3.5.1.1 Open System Reactor

The amount of chemicals required for each experiment was weighed out on a Mettler balance (accuracy ±0.001 g). The chemicals were poured into a large beaker and dissolved in one liter of distilled water. The solution was preheated to 55°C. Calcium sulfite solids, gypsum, and the solution were then added to the reactor. The slurry was agitated for at least 30 minutes. Meanwhile, the temperature of the water bath was set at 550C. The variable speed agitator was set at the desired rate. The desired initial pH at 55°C was obtained by adding 5 N sulfuric acid or 5 N sodium hydroxide. After the pH of the solution stabilized, the experiment was started by simultaneously inserting the oxygen sparging tube into the slurry and turning on the automatic burette dispenser. The temperature of the slurry was periodically recorded. During each experiment, four to ten slurry samples were taken and analyzed for total sulfite concentration by iodimetric titration. The slurry samples were then filtered and the filtrates were stored in the refrigerator for organic acid analyses by ICE or GC.

3.5.1.2 Closed System Reactor

The experimental procedures for the closed system were basically the same as those of the open system except for the following modifications:

1. The solution was sparged with nitrogen for about one hour to remove CO_2 from the system before starting the experiment.
2. Pure oxygen was fed over the surface of the reacting solution. Gas phase degradation products and unreacted oxygen were collected in a gas bomb for hydrocarbon analyses. The gas bomb was replaced periodically.
3. pH of the solution was controlled to be within ±0.02 by adding sulfuric acid or sodium hydroxide solution if necessary.

3.5.2 SODIUM SULFITE CLEAR SOLUTION SYSTEM

For the closed reactor and clear solution system, the experimental procedures were quite different from those of the slurry system. Two methods have been used for the clear solution system, i.e., continuous feeding and pH-stat methods.

3.5.2.1 Continuous Feed

Sodium sulfate (0.3 M) and organic acid (10 - 30 mM) were weighed and poured into the reactor with 1.0 liter distilled water. After the solution temperature stabilized at 55°C and CO_2 was depleted completely, a sodium sulfite solution with known concentration was fed continuously into the reactor and the oxygen was turned on. The sulfite oxidation rate was equivalent to the feedrate and the organic acid decarboxylation rate was obtained directly from the CO_2 evolution rate.

3.5.2.2 pH-Stat

This method is basically the same as with continuous feed except that sodium sulfite solution is added to the reactor as necessary to maintain constant pH. The oxidation rate could be obtained from the sodium sulfite titration rate.

3.6 ANALYTICAL METHODS

3.6.1 IODIMETRIC TITRATION

3.6.1.1 Total Sulfite

The slurry samples collected during each experiment were analyzed for their total sulfite concentration by iodimetric titration. One ml slurry sample was dissolved in approximately 30 ml of pH 6 acetate buffer solution, which was composed of 1 M sodium acetate and 0.05 M acetic acid. A known amount of excess iodine was added to the solution and then titrated with standard sodium thiosulfate using starch as an endpoint indicator. The same procedures were repeated for one ml distilled water instead of sample for blank test. The pH

6 buffer was necessary. Above pH 8.0, iodate (IO_3^-) was formed and reacted with thiosulfate to give sulfate rather than tetrathionate ($S_4O_6^{2-}$). Below pH 4.0, iodine oxidation by air and starch decomposition could affect the analysis. The concentration of sulfite present in the slurry solution was determined by use of the following equation:

$$C = M(B-S)/2/V \tag{3.5}$$

where

C = Concentration of sulfite, mole/liter

B = Volume of sodium thiosulfate used to titrate the blank, ml

S = Volume of sodium thiosulfate used to titrate the sample, ml

M = Concentration of the sodium thiosulfate, moles/liter

V = Volume of sample, ml

3.6.1.2 Dissolved Sulfite/bisulfite

The $[S(IV)]_d$ in a filtrate from a slurry sample was no longer of the original concentration. Two reactions would affect the concentration. One was the dissolution of calcium sulfite solids, resulting in overestimated $[S(IV)]_d$. The other was the air oxidation of sulfite, resulting in underestimated $[S(IV)]_d$.

The filtrate (≈20mℓ) of slurry sample was heated to 55°C and the pH of the solution was adjusted back to the original pH by air oxidation if the pH was too high or by adding sodium sulfite if the pH was too low. Since $[S(IV)]_d$ was very low (0.1 - 10 mM), 100μℓ microsyringe was used to measure the volume of iodine and thiosulfate solution. Then the procedures described in the above section were used to determine $[S(IV)]_d$, the dissolved sulfite/bisulfite concentration.

In the case of sodium sulfite clear solution, the sample was taken directly from the reactor and was added to an Erlenmyer flask containing adequate amounts of iodine solution and pH 6 buffer. No pH adjustment was necessary.

3.6.2 ION CHROMATOGRAPHY EXCLUSION (ICE)

A Dionex Model 14 Ion Chromatograph was used to analyze organic acids and their degradation products by ion chromatography exclusion (ICE). The system used a 9×250 mm separator column and a 4×280 mm suppressor column. The eluent was 0.02 to 0.1 mM HCl at 46 to 62.6 mℓ/hr. A sample loop with 0.5 mℓ was provided. To get reproducible results, the system was calibrated with organic acid standards before each analysis. A mixture of 0.05 to 0.1 mM of succinic, glutaric and adipic acid was separated successfully on the ICE using 0.1 mM HCl as the eluent (Figure xb.1 , Appendix B).

3.6.3 TOTAL CARBON ANALYZER (TOC)

An Oceanography 525 carbon analyzer was used to measure carbon concentration in filtered solution. Liquid samples (10 - 30 μℓ) were injected into the sample filament where organic materials were oxidized to carbon dioxide by pure oxygen with the aid of catalyst. The catalyst in the sample filament consisted of asbestos, cobalt nitrate, and manganese dioxide. The cobalt allowed the asbestos to hold up under heat for longer periods of time and the manganese dioxide was an effective oxidation catalyst. The detector was a Horiba PIR-2000 CO_2 analyzer. Adipic acid was used to prepare the standard solution for calibration. A calibration curve is given in Figure bx.2 in Appendix B.

3.6.4 GAS CHROMATOGRAPHY (GC)

A Varian 3700 Gas Chromatograph with a flame ionization detector was used to analyze organic acids and their degradation products. A six foot, 1/4 inch glass column packed with 100/120 chromosorb, 10% H_3PO_4 was used for both mono- and dicarboxylic acids.

Monocarboxylic (volatile) acids were determined by extraction of acidified solution with chloroform followed by injection of the chloroform phase. One mℓ chloroform and 0.1 mℓ 50% H_2SO_4 were added to 2 mℓ of aqueous sample. After shaking for a minute, the mixture was left standing for another 15 minutes before injection. Figure xb.3 in Appendix B gives the GC chromatogram of the esters of some monocarboxylic acids.

Dicarboxylic (nonvolatile) acids were methylated in aqueous solution before extraction. 2.0 ml of methanol and 0.5 ml of 50% H_2SO_4 were mixed with 1.0 ml sample and left overnight. 0.5 ml chloroform was then used to extract the methyl ester. Figure xb.4 in Appendix B gives the performance of the GC with these procedures.

Hydroxycarboxylic acids were too polar to be extracted into chloroform from aqueous solution. The following procedures were used for the analyses of hydroxycarboxylic acids:

1. Place 12 gram silicic acid in a 30 ml fritted-glass crucible and apply suction to pack the column.
2. Add H_2SO_4 to 5 ml sample to adjust pH to around 1.0.
3. Pour sample evenly on the top of the packed column. Apply suction until the last portion of the sample has entered the column.
4. Quickly add 100 ml methanol to the column and apply suction. Discontinue the suction just before the last portion of the reagent enters the column.
5. Concentrate the methanol solution to dryness by using a rotary evaporator at 40°C.
6. Wash the residue in the flask with methanol and adjust the total volume to 2.0 ml
7. Add 2 drops of concentrate H_2SO_4 and let sit overnight.
8. Inject 1.0 μℓ of the methanol solution into GC.

Table 3.1 GC Conditions for the Measurement of Organic Acids and Their Degradation Products

Components	Monocarboxylic	Dicarboxylic	Hydroxycarboxylic	Hydrocarbons
column	SP-1000	SP-1000	Tenax GC	Porapak Q
	6'×1/4", glass	6'×1/4", glass	6'×1/8", steel	6'×1/8", steel
Sample preparations	pH adjusted to 1 $CHCl_3$ extraction	pH adjusted to 1 methylation $CHCl_3$ extraction	pH adjusted to 1	-
Injector (°C)	190	190	300	180
FID (°C)	210	210	320	200
Oven Temp(°C)				
initial	110(4 min)	80(2 min)	150(3 min)	120
programming	10/min	20/min	20/min	-
final	160(5 min)	160(5 min)	250(3 min)	-

Both monocarboxylic and hydroxycarboxylic acids can be analyzed with a special column - Tenax GC by aqueous injection. The procedure for sample preparation is to acidify the aqueous sample to pH = 1. A six-foot, 1/8-in. Propak Q stainless steel column was used to analyze Hydrocarbon. 2 cc of gas sample at 1 atm was injected to GC. The GC conditions for the measurement of organic acids and their degradation products are summarized in Table 3.1.

3.6.5 GAS CHROMATOGRAPH-MASS SPECTROMETER (GC/MS)

A Finnigan 4023 Gas Chromatograph - Mass Spectrometer (GC/MS) with INCOS Data System was used to identify degradation products of organic acids.

The analytical procedures were the same as those for GC alone. The separation column had the same packing but different shape required to fit Finnigan 4023 GC/MS.

SECTION 4 SULFITE OXIDATION

4.1 SUMMARY

The oxidation rates in clear solution experiments were practically constant, probably due to very low agitation rate with resulting mass transfer control. Under mass transfer controlled conditions (with 1 mM Mn), the sulfite oxidation rate of calcium sulfite slurry increased as agitation rate increased and/or as reaction solution volume decreased if oxygen was fed to the reactor above the gas-liquid interface. On the other hand, if oxygen was fed to the reactor beneath the gas-liquid interface, the oxidation rate was not affected by reaction solution volume. Under kinetically controlled conditions, the oxidation rate of calcium sulfite slurry increased as pH decreased, primarily due to the effect of pH on the solubility of calcium sulfite. Sulfite oxidation was catalyzed by Fe, Mn, Co, and Cu and inhibited by thiosulfate and hydroxycarboxylic acids. Usually, the inhibition could be overcome by adding Mn and/or sulfate salts which increased dissolved S(IV). Thiosulfate had a threshold effect on sulfite oxidation in the presence of manganese, and the threshold concentration decreased as pH increased, probably due to the decrease of dissolved S(IV).

4.2 INTRODUCTION

In flue gas scrubbers, the degradation of organic acids is conjugated with the oxidation of S(IV). Therefore, the mechanism of S(IV) oxidation is the key to understanding the degradation of organic acids. This mechanism has been of considerable interest recently because of concern over atmospheric reactions of SO_2 and because of the effect of S(IV) oxidation on the performance of the most commonly used desulfurization technique, lime/limestone wet scrubbing.

The oxidation of S(IV) is so complex that there is no generally accepted mechanism, though there have been a great many studies on the subject over the past century (Westley, 1982). However, it is generally agreed that the oxidation of S(IV) is essentially free radical in nature (Altwicker, 1977). It has been known since the work of Titoff (1903) that the rate of oxidation of S(IV) in aqueous solution can be reduced to a negligible level by the use of very pure water and that the rates observed otherwise are due to catalysis by metal ions. Furthermore, it was observed that the addition of complexing agents inhibited the reaction (Huss et al., 1978). Therefore, it is apparent that a crucial step in this oxidation is the interaction of S(IV) with certain metal ions. The oxidation rate can also be enhanced by ultraviolet light (Mathews and Dewey, 1913). The latter will not be covered here in this work because of no light exposure in the FGD system.

The oxidation of S(IV) is catalyzed not only homogeneously but also heterogeneously (Martin, 1983). The oxidation is inhibited by many organic compounds, especially alcohols (Mathews and Weeks, 1917). The complex nature of the oxidation of S(IV), the diversity of rate laws (Hoffman and Jacob, 1983), and the nonreproducibility of the kinetic data all together make the universal mechanism impossible, and suggest the existence of parallel mechanisms.

4.3 RESULTS - SULFITE OXIDATION

The oxidation behavior of calcium sulfite slurry is complicated. In addition to aqueous chemical kinetics, the oxidation of calcium sulfite slurry has to deal with both gas-liquid and solid-liquid mass transfer including calcium sulfite dissolution and calcium sulfate crystallization. Both affect the concentration of dissolved S(IV) and therefore affect the sulfite oxidation rate, especially when the oxidation reaction is controlled kinetically. Since this work emphasized the degradation of organic acids, the detailed study of calcium sulfite oxidation is beyond the scope, and only a minor effort has been made to study sulfite oxidation, especially in the presence of organic acids. The results on sulfite oxidation and organic acid degradation are summarized in Tables 4.1 and 4.2. The raw data are listed in Appendix A.

4.3.1 EFFECTS OF AGITATION AND SOLUTION VOLUME ON SULFITE OXIDATION

The pH-Stat method (Prada, 1981) was used to study effects of agitation and reaction solution volume on sodium sulfite oxidation in the gas-tight closed reactor. The effect of agitation on the sulfite oxidation rate is given in Figure 4.1. Because of the presence of 1 mM Mn, the oxidation rate was controlled by the mass transfer of oxygen through the gas-liquid interface and higher agitation rate increased the mass transfer coefficient, $k_{\ell}A$.

The effect of reaction solution volume on sulfite oxidation rate under oxygen mass transfer controlled conditions is given in Figure 4.2. Even though the agitation rate was maintained constant at 800 rpm, the sulfite oxidation rate increased as reaction solution volume decreased. Oxygen dispersion into the solution was enhanced by decreasing the distance between the gas-liquid interface and the turbine impeller. The increase of gas-liquid contact area was observed qualitatively by the naked eye. Another set of experiments with air oxidation were performed and showed the same tendency as pure oxygen oxidation (Figure 4.2). However, the oxidation rate was about 50% less than expected. This could be due to the depletion of oxygen in the air bubbles.

Typical calcium sulfite oxidation behavior for the open system reactor at 1340 rpm is shown in Figures 4.3 and 4.4 for two different batches of cal-

Table 4.1 Summary of the Degradation of Organic Acids Conjugated with the Oxidation of Calcium Sulfite Slurry at 55°C

Run	pH	Oxidation Rate(M/hr)	Other Conditions (mM)	k_d (M^{-1})	Adipic
Acid (Open Reactor)					
AA1	5.5	0.33	1 Mn	0.61	
AA2	5.5	0.23	1 Mn, 11 Glycolic	0.55	
AA3	4.5	0.55	1 Mn	0.07	
AA4	4.5	0.01	1 S_2O_3	-	
AA5	4.5	0.42	1 S_2O_3, 1 Mn	0.11	
AA6	5.0	0.36	1 S_2O_3, 300 $MgSO_4$	0.08	
AA7	5.0	0.02	10 S_2O_3, 300 $MgSO_4$	-	
AA8	5.0	0.44	10 S_2O_3, 300 $MgSO_4$, 0.3 Mn	0.21	
AA9	5.5	-	10 S_2O_3, 1 Mn	-	
AA10	5.0	-	10 S_2O_3, 1 Mn	-	
AA11	4.5	-	10 S_2O_3, 1 Mn	-	
AA12	5.5	0.08	1 S_2O_3	-	
AA13	5.5	0.50	1 S_2O_3, 1 Mn	0.25	
AA14	5.5	-	3 S_2O_3, 1 Mn	-	
AA15	5.0	-	3 S_2O_3, 1 Mn	-	
AA16	4.5	0.45	3 S_2O_3, 1 Mn	0.12	
AA17	5.5	-	2 S_2O_3, 1 Mn	-	
AA18	5.0	0.52	2 S_2O_3, 1 Mn	0.18	
AA19	5.5	0.45	1.2 S_2O_3, 1.2 Mn	0.16	
AA20	5.5	0.50	0.5 S_2O_3, 1 Mn	0.28	
AA21	5.5	0.22	0.1 M_{11}	-	
AA22	5.5	0.47	3 Mn	~0	
AA23	5.5	0.47	3 Mn	0.20	
AA24	5.5	0.24	0.1 Mn	0.23	
Adipic Acid (Closed Reactor)					
NA 1	5.0	0.36		2.5	
NA 2	5.0	0.05		0.85	
NA 3	5.0	-		1.28	
NA 5	5.0	1.02	1 Mn, 1000 rpm	0.20	
NA 6	5.0	0.36	1 Mn	0.12	
NA 7	5.0	0.50	0.1 Mn	1.09	
NA 8	5.0	0.11	1 Tl	0.58	
NA 9	5.5	0.10	10 Tl	0.65	
NA 10	5.0	0.27	1 KI	0.14	
Glutaric Acid (Open Reactor)					
G 1	4.6	0.28		0.24	
G 2	5.5	0.006		3.34	
G 3	5.5	0.30	0.1 Mn	1.55	
G 4	5.5	0.30	0.1 Mn	1.57	
Glutaric Acid (Closed Reactor)					
NG1	5.0	0.22	1 Mn	0.23	
NG2	5.0	0.23	0.03 Mn	0.61	
NG3	5.0	0.19	0.03 Mn, 1 Fe	0.88	
NG4	5.0	0.48	3 Glutaric	1.01	
NG5	5.0	0.39	1 Glutaric	1.63	
NG7	5.0	0.56	300 NaCl	0.40	
NG8	5.0	0.38	100 NaCl	1.31	
NG9	5.0	0.09	30 NaCl	1.78	
NG10	5.0	0.13	-	0.67	

Table 4.1 (cont'd)

Run	pH	Oxidation Rate(M/hr)	Other Conditions (mM)	k_d (M^{-1})
NG11	5.0	0.11	-	0.69
NG12	5.0	0.09	0.03 Mn	-
NG13	5.0	0.39	1 Mn	0.50
NG14	5.0	0.36	10 Mn	0.08
NG15	5.0	0.45	5 Mn, 2 EDTA	0.21
NG16	5.0	0.04	600rpm	0.54
NG17	5.0	0.06	1000rpm	0.66
NG19-1	5.0	0.12	0.0018 Fe	0.65
NG19-2	5.0	0.12	0.0036 Fe	0.88
NG19-3	5.0	0.15	0.0054 Fe	1.19
NG20-1	5.0	0.23	0.009 Fe	1.26
NG20-2	5.0	0.31	0.018 Fe	1.99
NG21	5.0	0.24	0.054 Fe	0.84
NG22-1	5.0	0.05	-	0.22
NG22-2	5.0	0.10	0.1 $NaNO_3$	0.34
NG22-3	5.0	0.09	0.5 $NaNO_3$	0.59
NG22-4	5.0	0.07	1 $NaNO_3$	0.65
NG23-1	5.0	0.11	100 $NaNO_3$	0.48
NG23-2	5.0	0.44	100 $NaNO_3$, 1 Mn	0.33
NG24	5.0	0.02	50 $Ca(NO_3)_2$	0.79
NG25	5.0	0.35	50 $Ca(NO_3)_2$,1 Mn	0.32
NG26	5.0	0.03	20 $Ca(NO_3)_2$	0.74
NG27	5.0	0.43	80 $Ca(NO_3)_2$, 1 Mn	0.40
NG28	5.0	0.35	100$Ca(NO_3)_2$, 1 Mn	0.59
Glutaric Acid (Closed Reactor) Continuously Feeding of $CaSO_3$ Slurry				
NG 29	5.0	0.011*	1 Mn	3.5
NG 30	5.0	0.179*	1 Mn	1.1
NG 31	5.0	0.088*	1 Mn	1.3
NG 32	5.0	0.037*	0.018 Mn	2.1
* Feedrate of calcium sulfite slurry				
Succinic Acid(Open Reactor)				
S 1	4.5	0.56		0.51
S 2	4.5	0.69	1.0 Mn	0.02
S 4	4.5	0.41	0.3 Mn	0.03
S 5	4.4	0.54	0.1 Mn	0.45
S 6	4.5	0.30	0.2 Mn	0.38
β-Hydroxypropionic Acid (Open Reactor)				
HP 1	4.5	0.52	2.0 HP	0.21
HP 2	4.5	0.49	1.0 Mn	0.06
HP 3	4.5	0.06		-
HP 4	5.5	0.58	1.0 Mn	0.04
HP 5	4.5	0.06		-
Hydroxyacetic Acid(Open Reactor)				
HA 1	4.5	0.04	-	-
HA 2	5.5	0.74	1.0 Mn	0.01
HA 3	5.0	0.02	-	-
HA 4	5.0	0.06	0.1 Mn	-
HA 5	5.0	0.37	0.3 Mn	0.07
HA 6	5.5	0.35	2.0 HA, 1.0 Mn	0.37
NHA 1	5.0	0	-	-
NHA 2	5.0	0.30	0.1 Mn	0.57
NHA 3	5.0	0.12	11 Mn	0.11
NHA 4	5.0	0.19	0.1 Mn	0.59
NHA 5	5.0	0.12	0.03 Mn	0.71

Table 4.1 (continued)

Run	pH	Oxidation Rate(M/hr)	Other Conditions (mM)	k_d (M^{-1})
Dibasic Acid(Open Reactor)				
DBA 1	5.5	0.25		
DBA 2	5.5	0.38	1 Mn, $1S_2O_3$	
DBA 3	4.0	0.51	-	
DBA 4	5.0	0.19	-	
Formic Acid(Closed Reactor)				
NF 1	5.0	0.30	1 Mn	0.6
NF 2	5.0	0.06	0.1 Mn	1.5
Acetic Acid(Open Reactor)				
AC 1	5.5	0.36	1 Mn	0.31
Valeric Acid(Closed Reactor)				
V 1	5.5	0.20	0.1 Mn(open reactor)	1.9
NV 1	5.0	0.30	1 Mn	0.1
NV 2	5.0	0.40	0.1 Mn	0.7
Malonic Acid(Open Reactor)				
MA 1	5.5	0.40	0.3 Mn	0.4
Fumaric Acid(Open Reactor)				
F 1	5.5	0.21	1.0 Mn	2.4
Ethyleneglycol(Closed Reactor)				
NEG 1	5.0	0.04		0.97
NEG 2	5.0	0.32	1 Mn	0.25

Table 4.2 Summary of the Degradation of Organic Acids Conjugated with the Oxidation of Sodium Sulfite Clear Solution at 55°C

Run	Other Conditions (mM)	Sulfite Oxidation Rate(M/hr)	CO2 Evolution Rate(mM/hr)	$[S(IV)]_d$ (mM)	k_d (M^{-1})	k_{12} $(\times 10^3)$
Adipic Acid						
NA 11	pH 4.0	0.03	0.048	5.0	0.16	0.8
NA 12	pH 5.0	0.03	0.06	4.5	0.20	0.9
NA 13	pH 6.0	0.03	0.063	3.9	0.21	0.8
NA 14	pH 4.4, 1 Mn	0.01	0.023	1.2	0.23	0.3
NA 15	pH 4.9, 1 Mn	0.01	0.034	0.5	0.34	0.2
NA 16	pH 5.7, 1 Mn	0.01	0.051	0.5	0.51	0.3
NA 17	pH 3.9, 0.1 Fe	0.01	0.38	0.9	3.8	3.4
NA 18	pH 4.6, 0.1 Fe	0.01	0.35	1.0	3.5	3.5
NA 19	pH 5.2, 0.1 Fe	0.01	0.18	1.3	1.8	2.3
NA 20	pH 5.4, 0.1 Fe	0.01	0.08	1.8	0.8	1.4
NA 21	0.82 atm O_2	0.01	0.18	0.56	1.78	1.0
NA 22	0.62 "	0.01	0.20	0.7	2.02	1.4
NA 23	0.41 "	0.01	0.20	0.6	2.02	1.2
NA 24	0.20 "	0.11	0.17	0.6	1.72	1.0
NA 25	0.07 "	0.11	0.20	0.65	1.95	1.3
NA 26	0.65 atm O_2 0.1 Fe	0.01	0.36	1.0	3.6	3.6
NA 27	0.41 ", 0.1 Fe	0.01	0.32	1.0	3.2	3.2
NA 28	0.18 ", 0.1 Fe	0.01	0.36	1.0	3.6	3.6
NA 29		0.01	0.25	0.45	2.5	1.1
NA 30	0.1 Mn	0.01	0.16	0.45	1.6	0.7
NA 31	0.2 Mn	0.01	0.06	0.4	0.6	0.2

Table 4.2 (continued)

Run	Other Conditions (mM)	Sulfite Oxidation Rate(M/hr)	CO2 Evolution Rate(mM/hr)	$[S(IV)]_d$ (mM)	k_d (M^{-1})	k_{12} ($\times 10^3$)
NA 32	0.3 Mn	0.01	0.03	0.7	0.3	0.2
NA 33	1.0 Mn	0.01	0.03	1.0	0.3	0.3
NA 34	-	0.0082	0.1294	0.74	1.58	1.17
NA 35	-	0.024	0.196	1.21	0.82	0.99
NA 36	-	0.0085	0.182	0.50	2.14	1.07
NA 37	0.02 Mn	0.0085	0.176	0.50	2.07	1.04
NA 38	0.05 Mn	0.0092	0.114	0.50	1.24	0.62
NA 39	0.10 Mn	0.0092	0.080	0.50	0.87	0.43
NA 40	0.20 Mn	0.0092	0.057	0.50	0.62	0.31
NA 41	1.20 Mn	0.0092	0.034	0.50	0.37	0.19
Co2(SO4)3, Oxidation Rate = 0.00337 M/hr						
NA 42		0.00337	0.0257	1.07	0.76	0.81
NA 43	0.03 Co	"	0.0257	1.10	0.76	0.84
NA 44	0.1 Co	"	0.0257	1.00	0.76	0.76
NA 45	0.3 Co	"	0.0292	0.95	0.86	0.82
NA 46	1.0 Co	"	0.0350	0.95	1.04	0.99
NA 47	3.0 Co	"	0.0816	0.66	2.42	1.60
NA 48	10 Co	"	0.3614	0.31	10.7	3.30
NiSO4.6H2O, Oxidation Rate = 0.0050 M/hr						
NA 49		0.0050	0.0298	1.50	0.60	0.89
NA 50	0.1 Ni	"	0.0564	1.05	1.13	1.18
NA 51	1.0 Ni	"	0.1128	1.10	2.26	2.48
CuSO4, Oxidation Rate = 0.0060 M/hr						
NA 52		0.006	0.0803	0.65	1.34	0.87
NA 53	0.03 Cu	"	0.0903	0.59	1.51	0.89
NA 54	0.1 Cu	"	0.1054	0.53	1.76	0.93
NA 55	0.3 Cu	"	0.1255	0.48	2.09	1.00
NA 56	1.0 Cu	"	0.1832	0.43	3.05	1.31
NA 57	3.0 Cu	"	0.2158	0.37	3.60	1.33
TiO2, Oxidation Rate = 0.00368 M/hr						
NA 58	0.1 Ti	0.00368	0.0170	1.67	0.52	0.86
NA 59	0.3 Ti	"	0.0180	1.85	0.49	0.90
NA 60	1.0 Ti	"	0.0154	2.05	0.42	0.86
NA 61	3.0 Ti	"	0.0123	2.51	0.34	0.84
NaVO3.xH2O, Oxidation Rate = 0.00697 M/hr						
NA 62		0.00697	0.0298	2.58	0.43	1.10
NA 63	0.1 V	"	0.0410	2.09	0.59	1.23
NA 64	0.3 V	"	0.0513	1.94	0.74	1.43
NA 65	1.0 V	"	0.0564	1.81	0.81	1.46
NA 66	3.0 V	"	0.0616	1.74	0.88	1.54
Cr2(SO4)3, Oxidation Rate = 0.00657 M/hr						
NA 67		0.00657	0.037	1.75	0.56	0.99
NA 68	0.1 Cr	"	0.028	2.43	0.43	1.03
NA 69	0.3 Cr	"	0.027	2.53	0.40	1.02
NA 70	1.0 Cr	"	0.023	2.88	0.35	1.02
TlNO3, Oxidation Rate = 0.00612 M/hr						
NA 71		0.00612	0.0308	1.84	0.50	0.93
NA 72	0.1 Tl	"	0.0359	2.21	0.59	1.30
NA 73	0.3 Tl	"	0.0410	2.41	0.67	1.61
NA 74	1.0 Tl	"	0.0616	2.65	1.01	2.67

Table 4.2 (continued)

Run	Other Conditions (mM)	Sulfite Oxidation Rate(M/hr)	CO2 Evolution Rate(mM/hr)	$[S(IV)]_d$ (mM)	k_d (M^{-1})	k_{12} ($\times 10^3$)
Potassium Bromide, NA 75 - 79: Oxidation Rate = 0.0047 M/hr						
NA 75		0.0047	0.195	0.65	4.15	
NA 76	0.1 Br	"	0.174	0.62	3.71	2.3
NA 77	0.3 Br	"	0.154	0.61	3.28	2.0
NA 78	1.0 Br	"	0.123	0.57	2.63	1.5
NA 79	10 Br	"	0.021	0.45	0.44	0.2
Iodide, Oxidation Rate = 0.0047 M/hr						
NA 80		0.0047	0.109	1.34	2.31	1.0
NA 81	0.1 I	"	0.017	0.83	0.36	0.3
NA 82	0.3 I	"	0.008	0.59	0.16	0.1
NA 83-85: 30 mM Adipic Acid						
NA 83	0.15 Mn	0.0060	0.02	10.5	0.11	1.2
NA 84	0.15 Mn	0.0051	0.0225	6.15	0.16	0.96
NA 85	0.15 Mn	0.0047	0.040	1.15	0.34	0.39
NA 86-117: 20 mM ADIPIC ACID						
NA 86	2 Br	0.0036	0.0075	11.7	0.10	1.2
NA 87	2 Br	0.0034	0.0081	8.1	0.12	0.98
NA 88	2 Br	0.0032	0.0322	0.3	0.53	0.16
NA 89	2 Br	0.0031	0.0182	1.0	0.31	0.31
NA 90	0.01 Fe	0.0063	0.025	10.0	0.20	2.0
NA 91	0.01 Fe	0.0046	0.053	3.8	0.58	2.2
NA 92	0.01 Fe	0.0041	0.023	7.9	0.28	2.2
NA 93	0.005 Fe	0.004	0.048	2.6	0.58	1.5
NA 94	0.3 Mn	0.0052	0.016	2.9	0.16	0.46
NA 95	"	0.0052	0.014	3.8	0.14	0.55
NA 96	"	0.0055	0.014	6.0	0.13	0.79
NA 97	"	0.0058	0.013	8.1	0.12	0.96
NA 98	"	0.0055	0.029	1.0	0.27	0.27
NA 99	0.02 Mn	0.0049	0.022	4.48	0.23	1.02
NA100	0.05 Mn	0.005	0.023	4.58	0.24	1.09
NA101	0.07 Mn	0.0052	0.025	4.20	0.25	1.03
NA102	0.10 Mn	0.0043	0.023	3.43	0.28	0.96
NA103	0.15 Mn	0.0054	0.023	3.85	0.22	0.84
NA104	0.2 Mn	0.0054	0.019	4.45	0.18	0.8
NA 105-107 (0.005 Fe)						
NA105	0.0125 Mn	0.0042	0.041	2.5	0.48	1.20
NA106	0.0375 Mn	0.0042	0.040	2.4	0.48	1.16
NA107	0.087 Mn	0.0047	0.038	2.2	0.41	0.91
NA 108-112 (0.01 Fe)						
NA108	0.15 Mn	0.0047	0.063	1.79	0.68	1.22
NA109	0.2 Mn	0.0048	0.048	1.95	0.5	0.98
NA110	0.25 Mn	0.0047	0.037	1.88	0.41	0.77
NA111	0.2 Mn	0.0046	0.021	3.75	0.23	0.87
NA112	0.0 Mn	0.0046	0.065	0.9	0.72	0.65
NA 113-117 (0.15 Mn)						
NA113	0.0001 Fe	0.0078	0.026	3.88	0.17	0.66
NA114	0.0003 Fe	0.0075	0.025	3.96	0.18	0.70
NA115	0.001 Fe	0.0077	0.028	3.75	0.19	0.70
NA116	0.004 Fe	0.0081	0.033	3.73	0.21	0.78
NA117	0.0107 Fe	0.0077	0.033	3.7	0.22	0.82

Table 4.2 (cont'd)

Run	Other Conditions (mM)	Sulfite Oxidation Rate(M/hr)	CO2 Evolution Rate(mM/hr)	$[S(IV)]_d$ (mM)	k_d (M^{-1})	k_{12} ($\times 10^3$)
Glutaric Acid						
NG 33	3 Glutaric	0.043	0.008	20	0.06	1.2
NG 34	3 Glutaric	0.040	0.040	3.0	0.33	1.0
NG 35	3 Glutaric	0.036	0.058	1.4	0.54	0.8
NG 36	3 Glutaric	0.038	0.018	6.9	0.16	1.1
NG 37	3 Glutaric	0.043	0.040	3.1	0.31	1.0
NG 38	3 Glutaric	0.038	0.183	0.5	1.60	0.8
Hydroxyacetic Acid, Sodium Salt						
NHA 6		0.0040	0.0108	1.8	0.27	0.49
NHA 7	1 Fe	0.0069	0.0405	1.7	0.59	1.00
NHA 8	1 Fe, 1 Mn	0.0098	0.027	1.6	0.28	0.44
NHA 9	0.1 Mn	0.0074	0.0378	1.37	0.51	0.70
NHA 10	0.3 Mn	0.0076	0.029	1.0	0.38	0.38
NHA 11	1 Mn	0.0078	0.0162	0.75	0.21	0.16
Maleic Acid						
NM 1		0.0117	0.118	6.8	1.03	7.0
NM 2	0.1 Fe	0.0116	0.244	3.1	2.19	6.8
NM 3	0.1 Fe,0.03 Mn	0.0105	0.263	1.8	2.64	4.8
NM 4	0.1 Fe, 0.1 Mn	0.0121	0.173	3.0	1.52	4.6
NM 5	0.1 Fe, 0.2 Mn	0.0134	0.169	3.0	1.34	4.0
NM 6	0.1 Fe, 0.3 Mn	0.0140	0.157	2.9	1.20	3.5
NM 7	0.1 Fe, 1 Mn	0.0140	0.165	2.7	1.28	3.5
NM 8		0.0132	0.147	5.8	1.16	6.7
NM 9	1 Mn	0.0142	0.113	4.3	0.84	3.6
NM 10	1 Mn, 0.1 I	0.0142	0.113	4.3	0.84	3.6
NM 11	pH 6.0	0.0140	0.126	6.3	0.92	5.8
NM 12	0.1 Fe, "	0.0137	0.136	5.9	0.96	6.0
NM 13	0.1 Mn, "	0.0137	0.110	5.5	0.84	4.6
NM 14	0.2 Mn, "	0.0136	0.110	5.0	0.85	4.3
NM 15	0.3 Mn, "	0.0136	0.110	4.8	0.86	4.1
NM 16	1 Mn, "	0.0134	0.110	3.8	0.88	3.3
Sulfosuccinic Acid						
NSS 1		0.0134	0.034	1.3	0.26	0.3
NSS 2	0.1 Fe	0.0143	0.040	1.2	0.29	0.4
NSS 3	0.1 Fe, 1 Mn	0.0159	0.011	1.3	0.08	0.1
NSS 4		0.0177	0.017	3.76	0.10	0.4
NSS 5		0.0158	0.045	1.55	0.30	0.5
NSS 6	0.1 Fe	0.0158	0.055	1.14	0.37	0.4
Malic Acid						
NMO 1	0.1 Fe	0.0139	0.034	5.7	0.25	1.4
NMO 2	0.1 Fe, 1 Mn	0.0134	0.017	3.8	0.13	0.5
NMO 3	0.1 Fe, 1 Mn	0.0135	0.028	2.2	0.22	0.5
4-Hydroxybutyric Acid						
NHB 1	0.1 Fe	0.0151	0.013	4.4	0.09	0.4
NHB 2	0.1 Fe, 1 Mn	0.0171	0.007	2.4	0.04	0.1
NHB 3	0.1 Fe	0.0135	0.056	0.9	0.42	0.4
Salicylic Acid (2-Hydroxybenzoic Acid) (20 mM)						
NSA 1	1 Mn	0.0041	0.0303	2.71	0.13	0.4
3-Hydroxybenzoic Acid (20 mM)						
NOHB 1	1 Mn	0.0035	0.0352	1.67	0.18	0.3
Benzoic Acid (20 mM)						
NBZ 1	1 Mn	0.0049	0.151	1.48	0.56	0.8

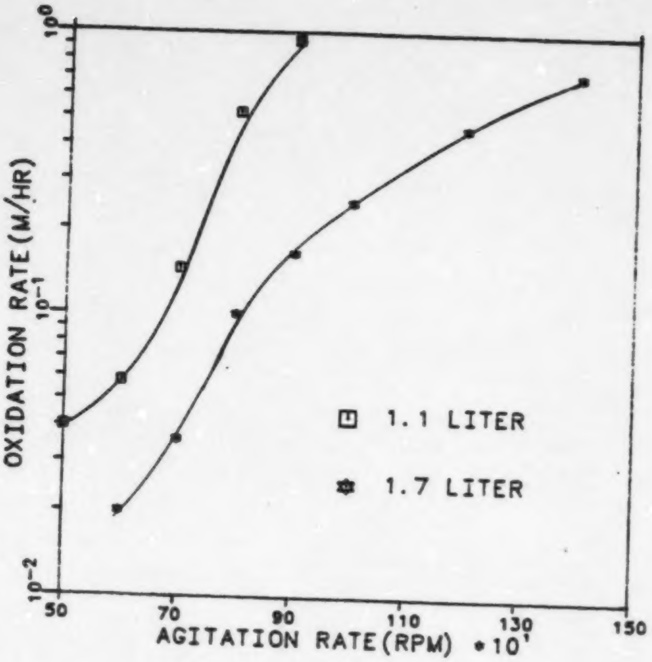

Figure 4.1: The Effect of Agitation on Calcium Sulfite Oxidation: closed reactor, 55°C, pH 5, oxygen fed above the solution

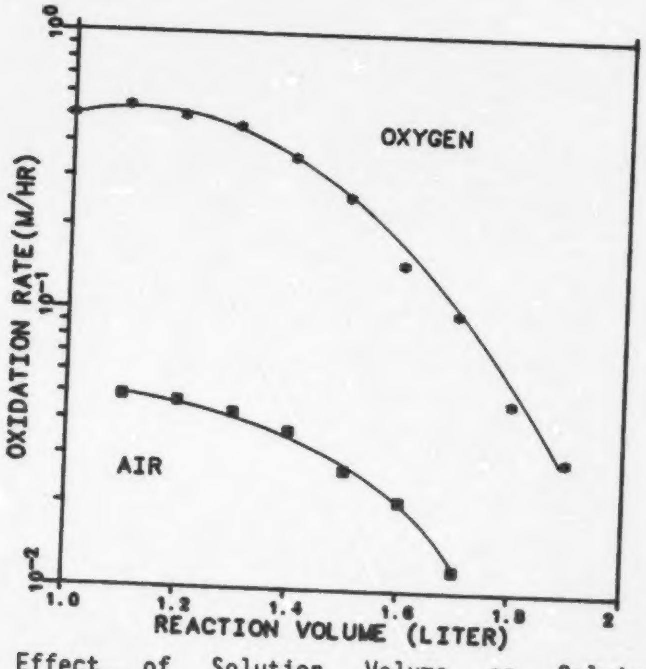

Figure 4.2: The Effect of Solution Volume on Calcium Sulfite Oxidation: closed reactor, 55°C, pH 5, oxygen or air was fed above the solution

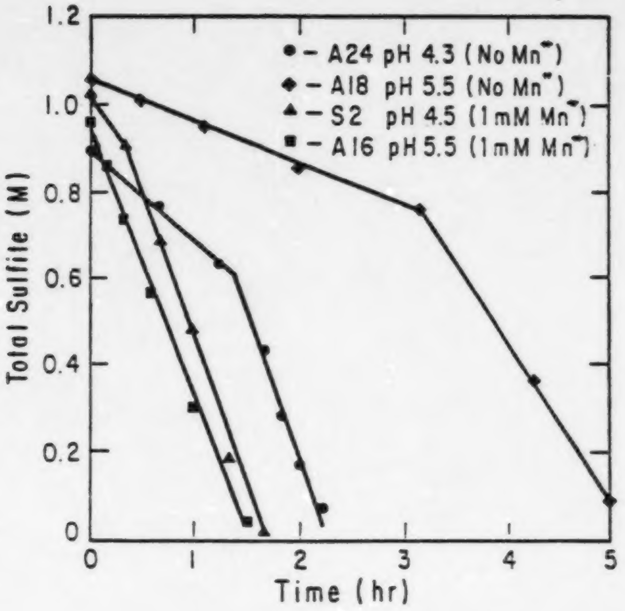

Figure 4.3: Calcium Sulfite Oxidation with high Mn, and/or Fe: open reactor, 55°C, pH 5, oxygen was fed into the solution

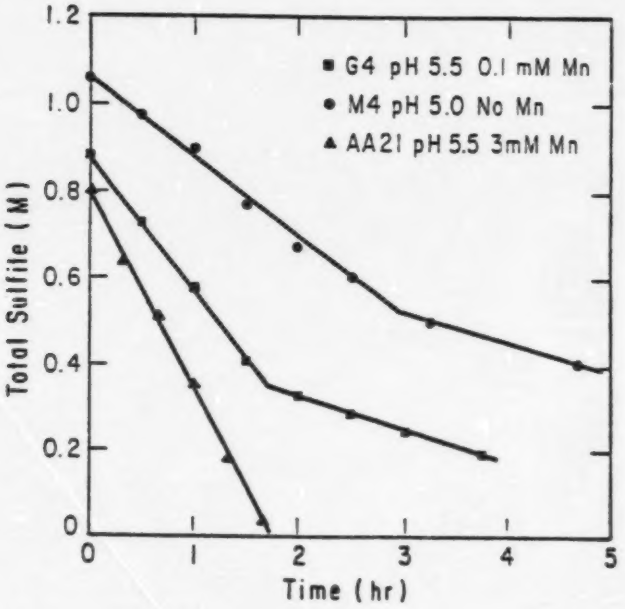

Figure 4.4: Calcium Sulfite Oxidation with low Mn and Fe: open reactor, 55°C, pH 5, oxygen was fed into the solution

cium sulfite prepared in the lab. Both figures indicate that the sulfite oxidation rate is approximately constant throughout the experiment in the presence of 1.0 mM or more $MnSO_4$. However, in the absence of Mn^{2+} or other added catalysts, the sulfite oxidation rate increased or decreased during the experiment. These observations are not explained by the effect of reaction solution volume. However, in these experiments, oxygen was introduced to the solution by inserting the sparger into the solution and the gas-liquid contact area per unit solution volume may not be changed throughout each experiment. Therefore, the sulfite oxidation rate with 1.0 mM Mn should not be affected by sampling and should be constant. The variation of the sulfite oxidation rate in the absence of added catalysts may be caused by the dissolution or coprecipitation of some catalyst impurities, probably iron, during calcium sulfite dissolution and calcium sulfate crystallization.

Figure 4.5 gives the calcium sulfite oxidation behavior for the closed system reactor where oxygen was fed to the reactor above the gas-liquid interface. The sulfite oxidation rate increased for the mass transfer controlled condition (high Mn), while it remained approximately constant for those experiments under kinetically controlled conditions. The data are consistent with the effect of reaction solution volume on sulfite oxidation mentioned above.

4.3.2 EFFECTS OF PH AND S(IV) ON SULFITE OXIDATION

The effect of pH on sulfite oxidation rates is not generally agreed upon but lower pH seems to decrease the rate more often than it increases the rate (Reinders and Vles, 1925; Turney, 1965). It has been claimed that SO_3^{2-} is more quickly oxidized than HSO_3^- (Hudson, 1980; Fuller and Christ, 1941), but there is no clear evidence for any difference in rates between the two species. However, for the case of calcium sulfite slurry oxidation, it is very clear that increasing pH results in decreasing oxidation rates under kinetically controlled conditions (Hsiang, 1981). The sulfite oxidation rate

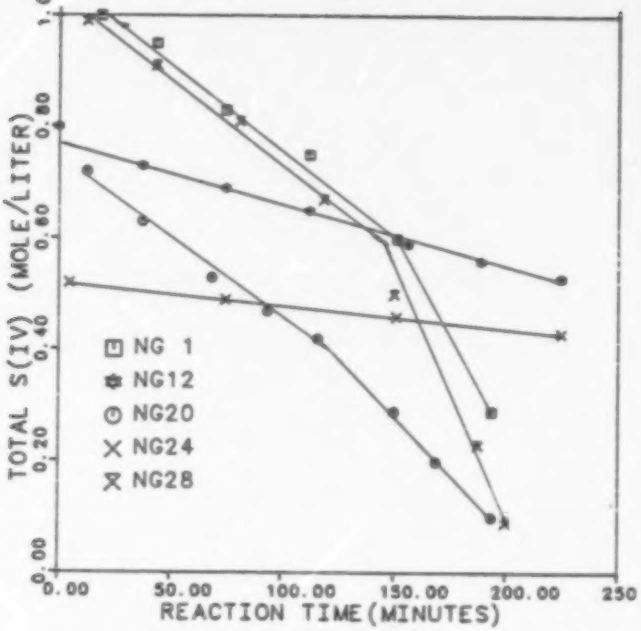

Figure 4.5: Calcium Sulfite Oxidation in the Closed Reactor: 55°C, pH 5, oxygen was fed above the solution

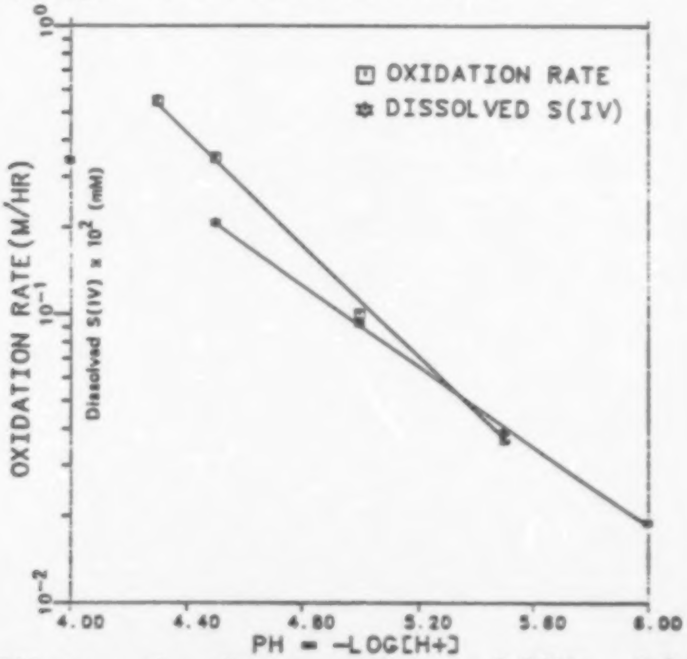

Figure 4.6: Effects of pH on Calcium Sulfite Solubility and Oxidation: 55°C, oxygen was fed above the solution

is not a function of pH in the presence of 1.0 mM Mn. Under this condition, the oxidation rate is probably limited by oxygen mass transfer rate.

The most probable explanation of the pH effect on calcium sulfite slurry oxidation is the variation of dissolved S(IV) caused by pH change. The solubility of calcium sulfite at 55°C is a strong function of pH as given in equations 3.1 and 3.3. The pKa value of HSO_3 is 7.2 (Yui, 1940). Therefore, the major species of S(IV) in the solution is HSO_3^- at pH ranging from 4.5 to 5.5. Figure 4.6 shows that the calcium sulfite oxidation rate is directly proportional to H activity, while dissolved S(IV) increases with H to the 0.7 power. Therefore, the variation of dissolved S(IV) explains most of the effect of pH upon calcium sulfite oxidation. The remaining effect of pH could be derived from protonation of intermediates or solubility of transition metals, especially iron.

4.3.3 CATALYSTS AND INHIBITORS - SULFITE OXIDATION

4.3.3.1 Transition Metal Ions

It has been shown that several transition metal ions catalyze sulfite oxidation (Ulrich, 1983). Among these transition metals, iron and manganese are of most interest because of their omnipresence in flue gas desulfurization systems. Manganese(II) sulfate and iron(II) Sulfate are used for the study.

The reaction order of $[Mn^{2+}]$ was reported to be dependent on either $[S(IV)]_d$ or $[Mn^{2+}]$. Martin (1983) found that, with 10 mM Mn^{2+}, it was second order in Mn with zero order in S(IV) when [S(IV)] was around 0.5 mM; it was first order in Mn with first order in S(IV) when [S(IV)] was below 1 μM. With 10 mM S(IV), the reaction order of Mn was found to change from second to first when $[Mn^{2+}]$ was above 10 mM (Ulrich, 1983).

Bassett and Parker(1951) found that Mn^{2+} salts had a pronounced catalytic effect on the rate of sulfite oxidation with almost complete suppression of dithionate formation, which was usually observed to be a byproduct of sulfite oxidation and can be explained by free radical mechanisms. They proposed a nonradical, polar mechanism to rationalize their observation. However, it cannot be entirely a polar mechanism. With 1 mM Mn, the oxidation is inhibited by thiosulfate, which is generally believed to be a free radical scavenger (AA 9-17, Table 4.1; Owens, 1984; Ulrich, 1983). Furthermore, the stability constant of the complex of Mn^{2+} and $S_2O_3^{2-}$ is not high enough to account for the inhibiting effect (Sillen and Martell, 1964).

The solubility of Fe^{2+} or Fe^{3+} is difficult to determine because of the many hydrolysis and precipitation reactions that can occur, some of which are slow in going to completion (Tamura et al., 1976; Gayer and Woontner, 1956; Siddall and Vasburgh, 1951: Leussing and Kolthoff, 1953). In addition, it is difficult to differentiate ferric from ferrous iron. At low pH, the reaction orders are observed to be first order to ferric and first order to S(IV). Above pH 4, ferric ion is not stable above 10^{-8} M (Martin, 1983). Fuzzi (1978) found that the rate law changed to second order in S(IV) and first order in ferric. One might expect no dependence on the amount of iron added to the solution if saturation were in effect, but Fuzzi observed a linear dependence of the rate on iron over the entire range. Ulrich (1983) found some catalytic effect of iron at pH 6 with iron concentration up to 0.1 mM. These observations strongly suggest that both ferric and ferrous are effective in catalyzing sulfite oxidation, and some form of colloidal iron hydroxide or small iron oxide particles are involved in the high pH catalysis.

The other transition metals of the first series in the periodic table were studied using the closed system reactor and sodium sulfite clear solution, including titanium (TiO_2), vanadium ($NaVO_3.xH_2O$), chromium ($Cr_2(SO_4)_3.12H_2O$), cobalt ($Co_2(SO_4)_3$, nickel ($NiSO_4.6H_2O$), and copper ($CuSO_4$). During these experiments, the oxidation rates were fixed by the feeding rate of sodium sulfite solution. However, the catalytic effects of these transition metals can be quantified by variation in S(IV) concentration (Table 4.2, Run # NA 42 - NA 74). Among these transition metals, only Co and Cu had significant catalytic activity. However, this experiment is not very rigorous for studying sulfite oxidation. According to Ulrich's work, Cr should also have significant catalytic effect, which could not be observed from Table 4.1. One possible reason was that there might be some interference of dissolved S(IV) measurement with Cr.

Halides, especially chloride, have been reported to be effective catalysts for aqueous sulfite oxidation at very low S(IV) concentration (Clarke and Radojevic, 1983). However, no catalytic effect was found for bromide or iodide up to 0.1 M under the conditions for this work. Chloride did catalyze sulfite oxidation at levels of 30 mM. No significant effect was found at lower concentration.

Thiosulfate was found to be a very powerful inhibitor. In the absence of Mn, 1 mM sodium thiosulfate is sufficient to inhibit the oxidation of calcium sulfite slurry even when the pH is as low as 4.5. Thiosulfate suffers degradation while it inhibits oxidation, and the oxidation rate recovers linearly back to the normal rate after complete degradation. At 30 mM Mn^{2+}, it was found that 1 molecule of thiosulfate prevented 39 molecules of S(IV) from oxidation (Ulrich, 1983). It was also reported that the degradation rate of thiosulfate was proportional to the square root of sulfite oxidation rate (Owens, 1984).

It appears that thiosulfate has a threshold effect on sulfite oxidation and the threshold concentration of thiosulfate in the presence of 1 mM Mn decreases as pH increases. More thiosulfate is required to inhibit sulfite oxidation at lower pH. When the thiosulfate concentration is lower than that threshold concentration it appears to have no inhibiting effect at all. Since pH would affect the dissolved sulfite concentration, it might be the S(IV) concentration, not the pH, that affects the threshold concentration of thiosulfate. This argument is supported by the fact that addition of $MgSO_4$ overcomes the inhibition of oxidation caused by thiosulfate (Table 4.1, Run # AA 1

- AA20). The introduction of magnesium sulfate would increase the dissolved S(IV) concentration according to equation 2.6.

It is well known that alcohols inhibit sulfite oxidation. It was proposed that SO_4^-, the free radical believed to be responsible for sulfite autoxidation, reacts with alcohol at a rate comparable to that of its termination (Hayon et al., 1972). Accordingly, it was found that hydroxycarboxylic acids were inhibitors of sulfite oxidation. β-Hydroxypropionic acid inhibited the oxidation when its concentration was 10 mM or higher. When the concentration was as low as 2 mM, the sulfite oxidation was not affected. Inhibition by β-hydroxypropionic acid was compensated for by 1.0 mM Mn even when the acid concentration was as high as 25 mM (HP1 - HP5, Table 4.1). The results with hydroxyacetic acid resembled those with β-hydroxypropionic acid (HA1 - HA5, Table 4.1).

SECTION 5 ORGANIC ACID DEGRADATION

Organic acid degradation is conjugated with sulfite oxidation. The oxidative degradation constant, k_{12} is increased by Fe and decreased by Mn and halides. Lower dissolved S(IV) magnifies these effects. k_{12} is defined as the ratio of the degradation rate of organic acid and the oxidation rate of S(IV) after being normalized with organic acid and dissolved S(IV) concentrations. A free radical mechanism is proposed and successfully rationalizes the experimental data.

Decarboxylation is the major degradation pathway. The major degradation products include carbon dioxide, smaller dicarboxylic acids, monodicarboxylic acids, hydroxycarboxylic acids, hydrocarbons, aldehydeacids, and other carbonyl compounds.

Hydroxyacids and sulfonated acids degrade slower than simple dicarboxylic acids by a factor of three while maleic acid, an unsaturated dicarboxylic acid,degrades an order of magnitude faster.

5.1 RESULTS - ORGANIC ACID DEGRADATION

Among the organic acid buffer additives, adipic and glutaric acids were studied most intensively. Adipic acid is effective, nonvolatile, and has been extensively tested up to commercial-scale. Glutaric acid is the major component of waste dibasic acid (DBA) from adipic acid production. Because of its low cost and comparable performance, DBA is currently dominating the market for buffer additives in flue gas desulfurization. The kinetic results presented below include adipic and glutaric acids only, unless specified.

5.1.1 ORGANIC ACID CONCENTRATION

For a rate equation of the general form,

$$\frac{-d[A]}{dt} = k_1[A]^n[R\bullet] \qquad (5.1)$$

$$\frac{-d[S(IV)]_t}{dt} = k_2[S(IV)]_d[R\bullet] \qquad (5.2)$$

the rate constant was determined using the integrated equations:

$$\frac{[A]_0^{1-n}-[A]^{1-n}}{1-n} = \frac{k_1}{k_2}\frac{1}{[S(IV)]_d}([S(IV)]_{t0}-[S(IV)]_t) \quad \text{if} \quad n \neq 1 \qquad (5.3)$$

$$\ln\frac{[A]_0}{[A]} = \frac{k_1}{k_2}\frac{1}{[S(IV)]_d}([S(IV)]_{t0}-[S(IV)]_t) \quad \text{if} \quad n = 1 \qquad (5.4)$$

where subscript 0 denotes initial condition. The reaction order of organic acid can be checked with the consistency of k_1/k_2 or k_{12} by varying n from 0.5 to 1 while changing the concentration of organic acid. Slurry experiments were performed with glutaric acid varying from 1 to 10 mM at pH 5.0 and 55°C with 0.03 mM Mn. $k_{12}/[S(IV)]_d$ from slurry experiments for different assumed order are presented in Table 5.1. The dissolved S(IV) was assumed to be constant for each experiment. Therefore, the values reported in Table 5.1 reflect the change of apparent k_{12}. A reaction order of 0.9 seems to give the best fit of the experimental data. However, first order is acceptable in this concentration range. For convenience, all following work assumes first order in organic acid. The oxidative degradation rate constant, k_{12} obtained in this manner may be a weak function of organic acid concentration.

The kinetic model proposed by Rochelle (Meserole et al., 1979) suggests that the organic acid degradation rate should be directly proportional to the organic acid concentration (eq. 2.5). Terry et.al. (1982) found empir-

Table 5.1 The Ratio of Oxidative Degradation Rate Constant, k_{12} to Dissolved S(IV) Calculated with Different Assumed Reaction Order of Glutaric Acid, Slurry, Closed Reactor at 55°C, pH 5

		$k_{12}/[S(IV)]_d(M^{-1})$				
Run	Conc(mM)	n=0.50	n=0.75	n=0.80	n=0.90	n=1.00
NG 5	1	1.1	1.1	1.2	1.3	1.2
NG 4	3	1.7	1.4	1.3	1.3	1.3
NG10	10	3.6	1.6	1.5	1.4	1.2
NG11	10	3.2	1.8	1.6	1.3	1.1

Table 5.2 Steady State Solution Composition in CaSO3 Slurry as a Function of pH Closed Reactor, 55°C, no Organic Acid

pH	Fe*	Mn**	$[S(IV)]_d$	Sulfite Oxidation
—	(mM)	(mM)	(mM)	Rate_(M/hr)
4.0	0.15	0.43	34.2	0
4.0	0.13	0.43	27.0	0.5
4.5	0.12	0.45	24.8	0
4.5	0.12	0.46	14.5	0.5
5.0	0.02	0.46	9.3	0
5.0	0.02	0.46	5.9	0.5
5.5	<0.01	0.47	3.9	0
5.5	<0.01	0.46	1.3	0.5

* 0.1 mM was added

** 0.5 mM was added

ically that the degradation rate was 0.55 order in adipic acid. However, their rate expression (eq. 2.8) is not directly comparable with the form used by the author.

5.1.2 SULFITE OXIDATION RATE

As discussed in section 2.2.1, when conjugated with sulfite oxidation, the rate of organic acid degradation can be expressed in terms of k_{12}. The degradation rate of organic acid should supposedly be proportional to sulfite oxidation rate and inversely proportional to $[S(IV)]_d$. The oxidative degradation rate constant symbolized as k_{12}, should be independent of $[S(IV)]_d$ and sulfite oxidation rate. Two experiments were performed in the closed reactor system with clear solution to check the effect of sulfite oxidation rate on organic acid degradation. Sulfite oxidation rate was controlled by varying the feedrate of sodium sulfite solution while keeping the pH 5.0 with dilute sulfuric acid or sodium hydroxide. When the oxidation rate changed from 0.0082 to 0.024 M/hr, $[S(IV)]_d$ changed from 0.74 to 1.2 mM and the CO_2 evolution rate, which was assumed to be the same as organic acid degradation rate under these conditions, changed from 0.13 to 0.20 mM/hr, while k_{12} only changed from 1.17×10^{-3} to 0.99×10^{-3}. In slurry experiments, the sulfite oxidation rate is around 1 M/hr, that is around 100 times faster than the aforementioned oxidation rate. With the introduction of estimated dissolved S(IV), k_{12} with the same order of magnitude could be obtained. Therefore, organic acid degradation rate is proportional to the oxidation rate of S(IV). Terry et al. (1982) correlated the degradation rate of adipic acid to be 1.185 power in percent oxidation, which is the ratio of sulfite oxidation rate to SO_2 absorption rate (eq. 2.8).

5.1.3 PH AND DISSOLVED SULFITE CONCENTRATION

A number of slurry experiments suggest that the degradation rate increases with increasing pH (Figure 2.2). However, in the slurry experiments the concentration of dissolved S(IV), $[S(IV)]_d$, is a strong function of pH as given in Figure 4.6 and also suggested by equation 3.1. Additional slurry experiments were performed to vary $[S(IV)]_d$ by adding soluble calcium to the solution (NG 24-28, Table 4.1). With the addition of soluble calcium salts, $[S(IV)]_d$ will decrease because of the equilibrium given in equation 3.1. Calcium nitrate was used to control $[S(IV)]_d$ because of the insignificant effect of sodium nitrate on $k_{12}/[S(IV)]_d$ (NG 22-23, Table 4.1). The results indicated that k_{12} increases as the amount of calcium nitrate added to the system increased (NG 24-28, Table 4.1).

To get a quantitative relationship between $k_{12}/[S(IV)]_d$ and $[S(IV)]_d$, sodium sulfite instead of calcium sulfite was oxidized for better control of $[S(IV)]_d$. In the absence of Fe or Mn, Figure 5.1 shows that the ratio $k_{12}/[S(IV)]_d$ is inversely proportional to $[S(IV)]_d$, consistent with a constant value of k_{12}.

In addition to affecting $[S(IV)]_d$, pH also affects the distribution of sulfite and bisulfite and the degree of protonation or dissociation of organic acids, which might be important in the degradation kinetics. Additional clear solution experiments were performed to show that k_{12} was not a function of pH for three different catalyst environments (Figure 5.2). At low $[S(IV)]_d$, k_{12} was practically constant with 1 mM Mn and without catalysts, but decreased as pH increased above 5.0 with 0.1 mM Fe. The decrease of k_{12} with 0.1 mM Fe was apparently caused by iron precipitation at high pH. Table 5.2 indicates that the solubility of ferrous solids decreases as pH increases while the solubility of manganese solids is greater than 1 mM and is not affected by pH, at least for the pH range: 4 - 6.

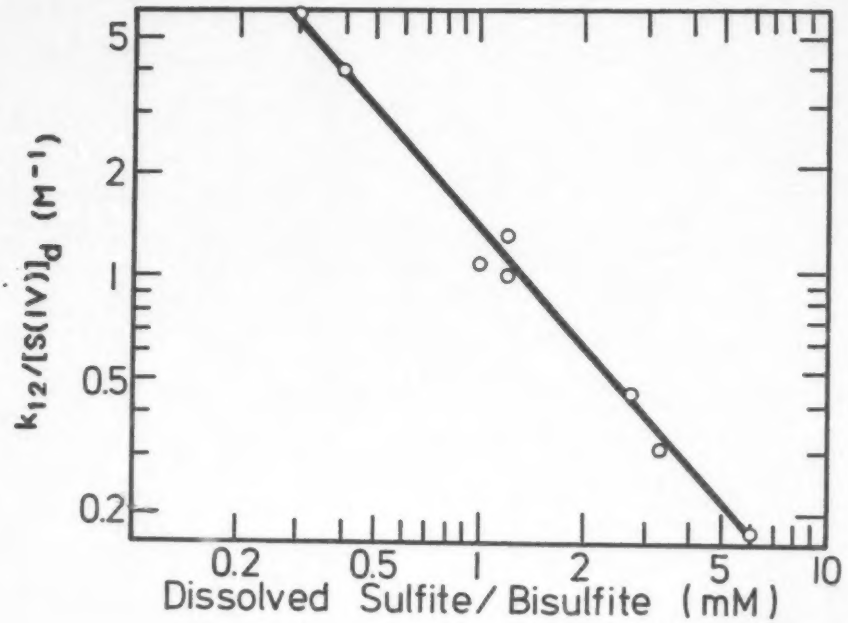

Figure 5.1: Effect of Dissolved S(IV) on the Degradation of Glutaric Acid: sodium sulfite solution, closed reactor, 55°C, pH 5.0

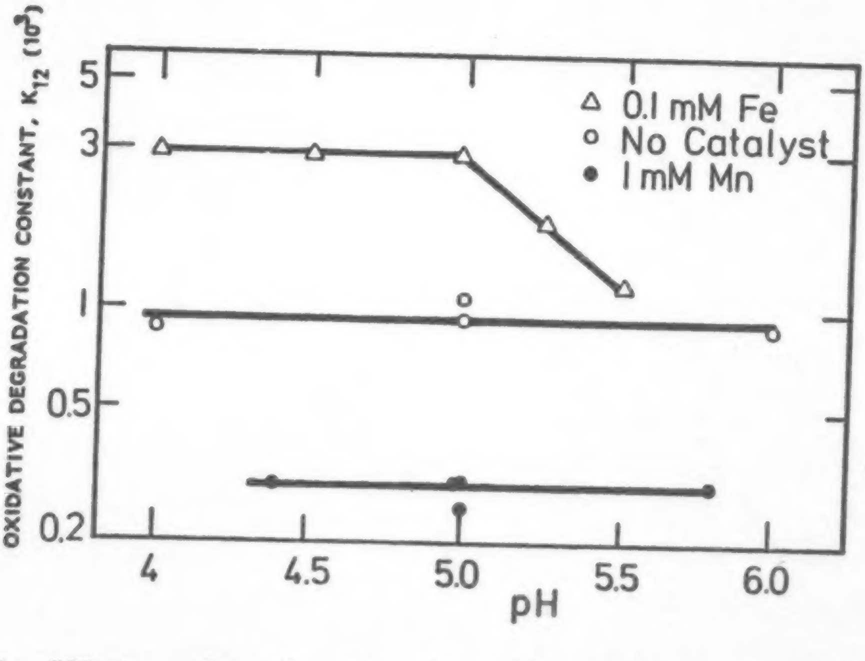

Figure 5.2: Effect of pH on the Degradation of Glutaric Acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1 mM

5.1.4 OXYGEN

The major pathway of organic acid degradation is probably decarboxylation. Both monocarboxylic and dicarboxylic acids were observed to be degradation products of dicarboxylic acid. Oxygen should be required to generate a smaller dicarboxylic acid. With slurry experiments, in the presence of 1 mM Mn, the dissolved oxygen would be practically zero because sulfite oxidation is controlled by mass transfer. However, under these conditions the major degradation product of adipic or glutaric acids was a dicarboxylic acid with one less carbon. Therefore, manganese must play some special role in carrying oxygen and transfering it to the precursor of dicarboxylic acid, or both oxidation and degradation occur at the interface where oxygen is saturated.

Figure 5.3 shows that there is no effect of P_{O2} on k_{12} with or without addition of Fe or Mn. Experimentally, P_{O2} was controlled by mixing oxygen with nitrogen. Therefore, the reaction order of oxygen in degradation and oxidation reactions should be equal and the effects cancel out each other. It was noticed, as in last section, that k_{12} is a strong function of the catalyst environment. The catalytic effect of iron and the inhibiting effect of manganese will be discussed in the following section. These experiments indicated that different values of k_{12} were obtained for different catalyst environment, but that k_{12} is generally independent of pH or P_{O2}.

5.1.5 TRANSITION METALS

It was shown that k_{12} was strongly affected by the catalyst environment. Among the catalysts, manganese and iron are of more interest because of their omnipresence in FGD systems.

Slurry experiments using $CaSO_3$ solids containing low iron impurities show that $k_{12}/[S(IV)]_d$ was more or less proportional to the square root of the concentration of iron ranging from 0.002 to 0.02 mM (Figure 5.4). Slurry

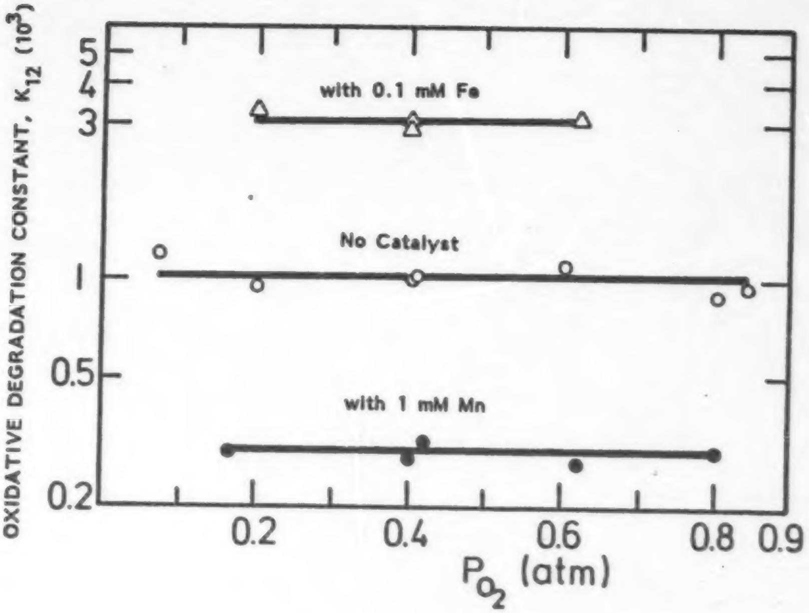

Figure 5.3: Effect of Oxygen on the Degradation of Glutaric Acid: sodium sulfite solution, closed reactor, 55°C, dissolved S(IV) ~1mM

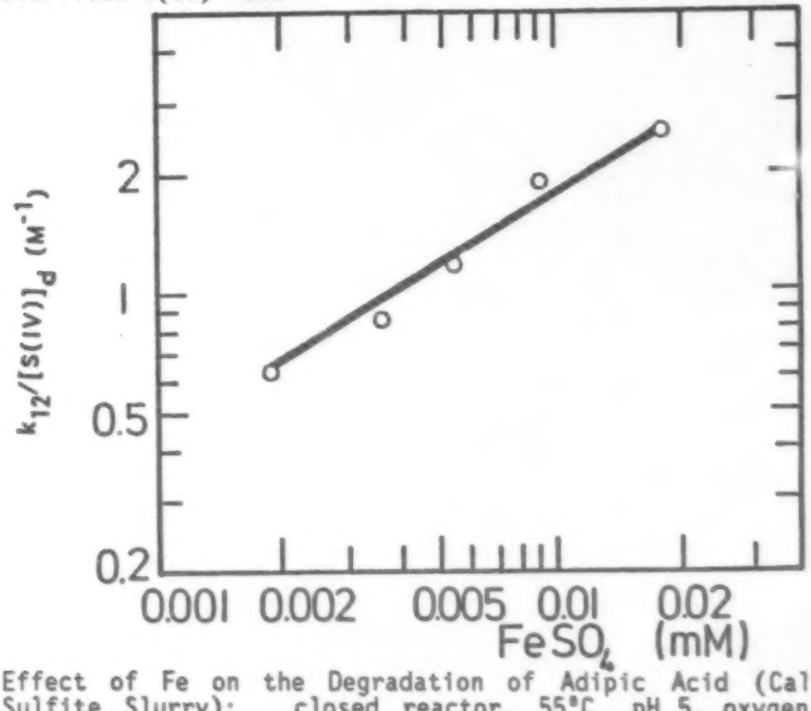

Figure 5.4: Effect of Fe on the Degradation of Adipic Acid (Calcium Sulfite Slurry): closed reactor, 55°C, pH 5, oxygen was fed above the solution

experiments with varying Mn concentration were less quantitative but demonstrate reduced oxidative degradation rate constant at higher Mn (Figure 5.5).

After careful examination with clear solution experiments, it was found that it was the ratio $[Fe]/[S(IV)]_d$ (Figure 5.6) or $[Mn]/[S(IV)]_d$ (Figure 5.7) that controlled k_{12}. In Figure 5.7, a 0.0007 mM background iron is assumed according to the correlation result which will be discussed later.

The remaining transition metals in the first series (except Sc and Zn) were also studied with sodium sulfite solution (NA 42-74, Table 4.2). Among these, Co, Ni, and probably Cu appear to catalyze organic acid degradation while Ti, V and Cr were inert (Table 5.3).

Slurry experiments showed minor inhibiting effect of thallium ($TlNO_3$) on the degradation of organic acid (NA 8-9, Table 4.1), which was not detected in the sodium sulfite solution system probably because of the interference of dissolved S(IV) measurement.

5.1.6 THIOSULFATE

Thiosulfate was recognized as an oxidation inhibitor in the early work by Tennessee Valley Authority (TVA) (1972), as was discussed in section 4.3.3.3. Being consumed while inhibiting sulfite oxidation, thiosulfate appears to function as a free radical scavenger rather than a complexing agent of metal ions or S(IV). It was observed that the rate of oxidation will be recovered after complete degradation of thiosulfate (Owens, 1984). But the degradation of organic acid does not occur when the degradation of thiosulfate (or the inhibition of S(IV) oxidation) is proceeding. A possible explanation of this inhibition of organic acid degradation is the high activity of thiosulfate towards the free radical attacking organic acids.

Large additions of thiosulfate stopped not only the oxidation of S(IV) but also the degradation of organic acid. The amount of thiosulfate needed to suppress the oxidation of S(IV) is proportional to the concentration of dis-

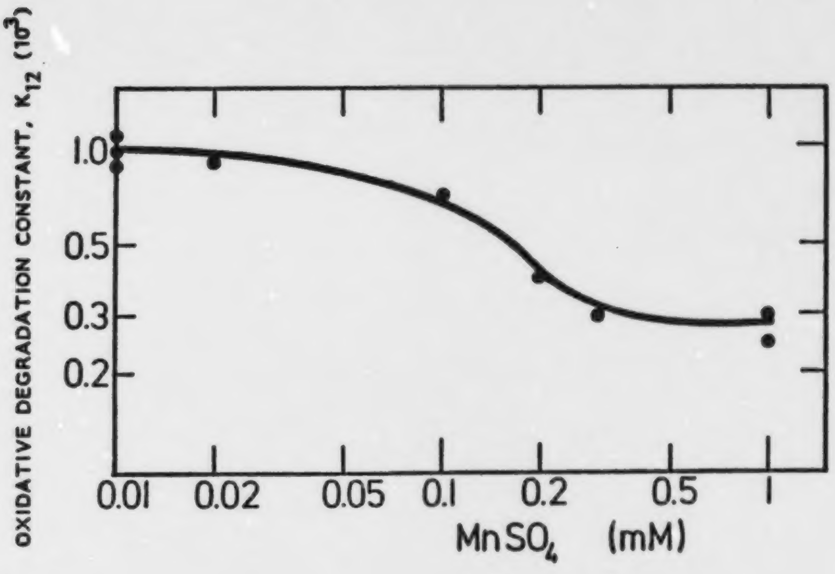

Figure 5.5: Effect of Mn on the Degradation of Adipic Acid (Calcium Sulfite Slurry)

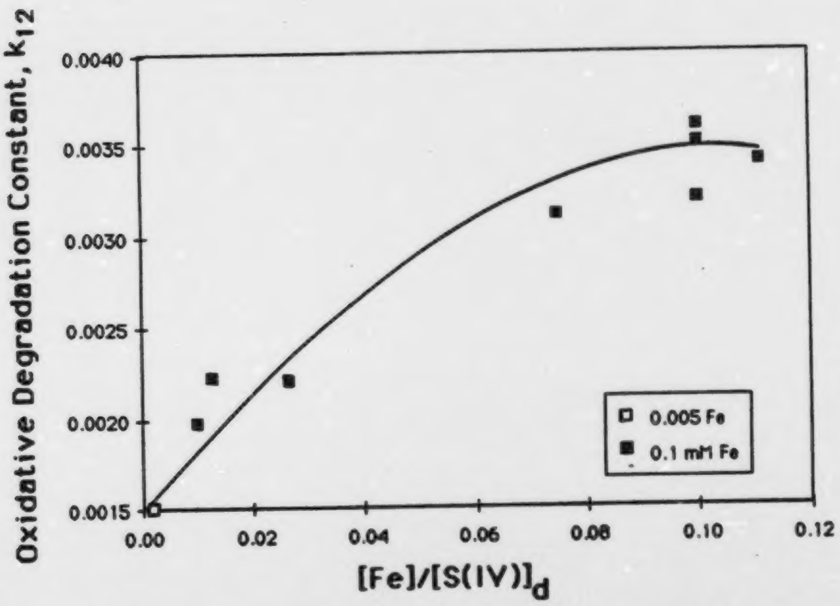

Figure 5.6: Effect of Fe on the Degradation of Adipic Acid (Sodium Sulfite Solution): closed reactor, 55°C, pH 5, oxygen was fed above the solution

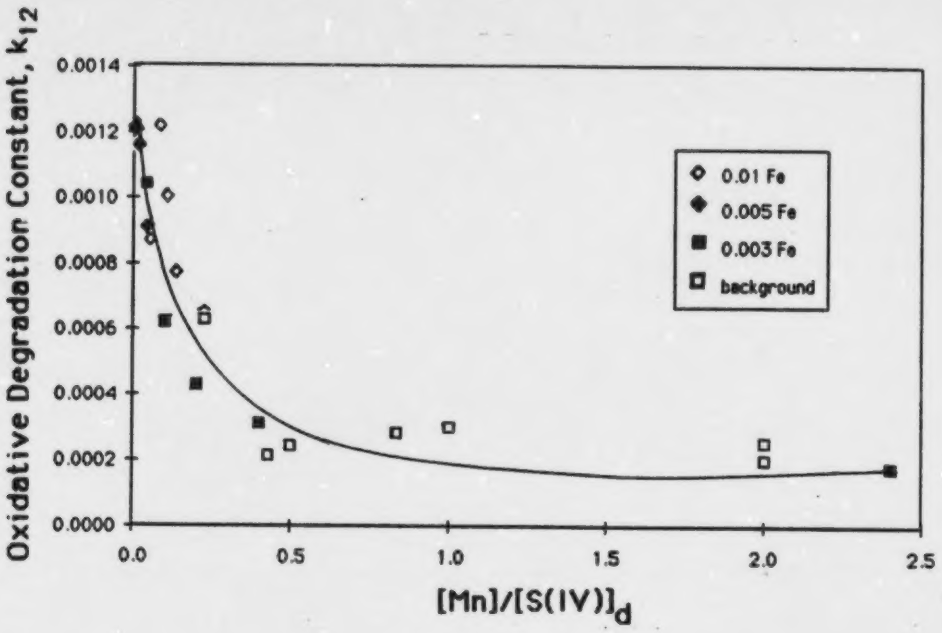

Figure 5.7: Effect of Mn on the Degradation of Adipic Acid (Sodium Sulfite Solution): closed reactor, 55±C, pH 5, oxygen was fed above the solution

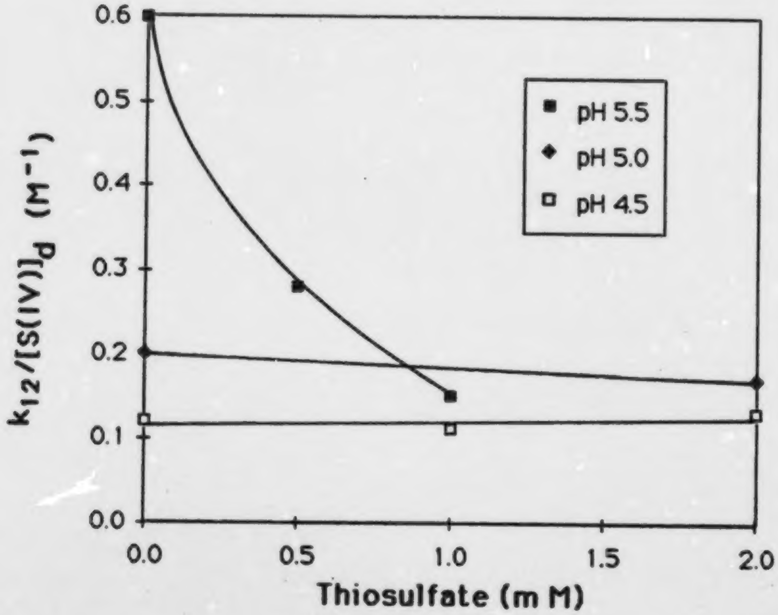

Figure 5.8: Thiosulfate Effect on the Degradation of Adipic Acid: calcium sulfite slurry, open reactor, 55°C, pH 5, oxygen was fed into the solution

Table 5.3 Effects of Transition Metals on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Conc (mM)	Oxidative Degradation Constant, $k_{12} \times 10^3$					
	Co	Ni	Cu	Ti	V	Cr
0	0.81	0.89	0.87	0.86	1.10	0.99
0.03	0.84	-	0.89	-	-	-
0.1	0.76	1.18	0.93	-	1.23	1.03
0.3	0.82	-	1.00	0.90	1.43	1.02
1.0	0.99	2.48	1.31	0.86	1.46	1.02
3.0	1.60	-	1.33	0.84	1.54	-
10.0	3.30	-	-	-	-	-
OXIDATION STATES	2,3	2,3	1,2	3,4	2,3,4,5	2,3,6

Table 5.4 Effects of Halide on k_{12} in Sodium Sulfite Solution by CO_2 Evolution from 10 mM Adipic Acid at pH 5.0, 55°C

Oxidative Degradation Rate Constant, $k_{12} \times 10^3$

Conc.(mM)	KCl	KBr*	KI*	$MnSO_4$
0	1.0	2.7	3.1	1.0
0.1	-	2.3	0.1	0.7
0.3	-	2.0		0.3
1	-	1.5		0.3
10	-	0.2		
30	0.8			
100	0.6			
300	0.3			

* with 1.0 mM Fe

solved S(IV) (Table 4.1). Therefore, the effect of thiosulfate on the degradation of organic acid could not be studied without the addition of an oxidation catalyst such as Mn or sulfate salts which increase $[S(IV)]_d$ to overcome the inhibition caused by thiosulfate. Figure 5.8 gives the ratio, $k_{12}/[S(IV)]_d$, for adipic acid at pH 4.5 to 5.5 with 1 mM Mn in calcium sulfite slurry at 55°C as a function of sodium thiosulfate. At pH 4.5 and 5.0, thiosulfate up to 2 mM had no significant effect on $k_{12}/[S(IV)]_d$. However, at pH 5.5, 1 mM thiosulfate reduced $k_{12}/[S(IV)]_d$ from 0.6 to 0.15 M^{-1}. The apparent pH effect could be due to $[S(IV)]_d$ variation caused by pH change in the calcium sulfite slurry. Owens (1984) found that more thiosulfate was required to inhibit oxidation for high dissolved S(IV), probably due to the competition for the active radical between S(IV) and thiosulfate. This is consistent with the observation that it is easier to overcome the inhibition at lower pH, for calcium sulfite slurry system. The degradation rate of thiosulfate, according to Owens (1984) is faster than that of adipic or glutaric acid by three orders of magnitude. The inhibiting effect of thiosulfate on the degradation of organic acid is probably due to the low dissolved S(IV) at pH 5.5. Reactive free radicals in an environment of low dissolved S(IV) have a significantly higher probability to react with thiosulfate rather than organic acid. This effect is not very strong in the presence of high dissolved S(IV) because of the competition of S(IV) and thiosulfate.

5.1.7 HALIDES

It has been proposed that high concentration of chloride (0.6 - 3 M) can be used in wet scrubbers to suppress the decomposition of the carboxylate salts during oxidation of sulfite and bisulfite (UK patent application GB2 082 159 A). In this section, chloride, bromide and iodide experiments at much lower concentration will be reported.

It was observed that NaCl varying from 0.03 to 0.3 M decreased k_d of glutaric acid at pH 5.0 and 55°C in calcium sulfite slurry from 1.6 to 0.4 M^{-1} (NG 7-9, Table 4.1).

Chloride, bromide, and iodide experiments were performed with sodium sulfite clear solution at pH 5.0 and 55°C. Table 5.4 shows that in the presence of 1 mM Fe, 10 mM NaBr reduced k_{12} from 2.7×10^{-3} to 0.2×10^{-3} while only 0.3 mM NaI reduced k_{12} from 3.1×10^{-3} to 0.1×10^{-3}. Chloride has no significant effect until its concentration is greater than 0.1 M. Therefore, the efficiency in suppressing organic acid decomposition is in the following order: $I^- > Br^- > Cl^-$.

The inhibiting effects of halides are a strong function of dissolved S(IV). As indicated in Table 4.2, the inhibiting effect of 2 mM Br (NA 86-89) is greater with reduced dissolved S(IV).

5.2 DEGRADATION PRODUCTS

The degradation products of adipic acid result from successive decarboxylation followed by oxidation (Figure 2.1). The gaseous products - CO_2 and hydrocarbons - represent loss of useable buffer. On the other hand, the products in solution - monocarboxylic and dicarboxylic acids - are useful buffers and represent only partial loss of adipic acid (Rochelle, 1982).

The expected degradation products of adipic acid, including monocarboxylic acids, dicarboxylic acids, and hydrocarbons were identified and quantified directly from GC. GC/MS was used to identify more complicated products. Among the degradation products, glutaric semialdehyde (4-formyl butyric acid) was not identified directly from GC/MS because of the lack of a reference mass spectrum. The identification of glutaric semialdehyde is discussed in Appendix C.

Table 5.5 gives a summary of the degradation products identified and tentatively quantified in experiments with low Mn (≤ 0.1). This table also

Table 5.5 Degradation Products from 80% Degradation of 10 mM Adipic Acid in Calcium Sulfite Slurry with 0.1 mM Mn at pH 5.0, 55°C in Terms of the Percentage of the Initial Concentration (mM C)

	Di-carboxylic	Mono-carboxylic	Hydroxy-carboxylic	Hydro-carbons	Others
C6	Adipic (20)				Tetrahydro 2,5 furan Dicarboxylic(*)
C5	Glutaric (1.5)	Valeric (0.7)	5-Hydroxyvaleric (2.5)		Glutaric Semialdehyde (6.7) 4-Oxopentanoic (0.3)
C4	Succinic (0.1)	Butyric (0.4)	4-Hydroxybutyric (2.5)	Butane (1.0)	Succinic Semialdehyde (*) Furane (0.6)
C3	Malonic (2.3)	--		Propane (*)	
C2		--		Ethane (*)	
C1		Formic (2.0)		Methane (*)	Formaldehyde (*) CO_2(49)

* less than 0.1%

Table 5.6 The Effect of Manganese on the Liquid Phase Degradation Products Distribution of Adipic Acid*

Products	AA21 0.1Mn(%C)	AA23 3 Mn(%C)
Valeric	0.9	8.7
Butyric	0.5	0.4
422	6.9	0.4
Glutaric	4.3	7.8
Succinic	1.6	0.6
Malonic	2.9	-
Glutaric Semialdehyde	24.2	0.7

* on the basis of degraded acid carbon

gives a composite of the results from actual runs to estimate a material balance for a hypothetical experiment with 80% degradation of 10 mM adipic acid at pH 5.0 with low Mn. About 90% of the initial carbon can be accounted for. Almost half of the carbon is lost as CO_2. The production of CO_2 is probably a function of fraction degradation and is discussed in more detail in Appendix D. The other important degradation products are glutaric semialdehyde, 5-hydroxyvaleric acid, 4-hydroxybutyric acid, and formic acid. The varieties of degradation products are the expected results via a free radical reaction. In a closed-loop scrubber system, hydroxycarboxylic acids and glutaric semialdehyde may accumulate because of the presence of hydroxyl and sulfonyl groups which were found to decrease degradation.

5.2.1 PRODUCT DISTRIBUTION

In the absence of Mn, there is less production of glutaric and succinic acids (Jarvis et al, 1981). Table 5.6 illustrates the effect of Mn on the degradation product distribution. Because of different degree of degradation and the different degradation rates of the products, this table gives only qualitative information on relative abundance of the degradation products. In the volatile products, an unknown 422 (GC retention time in seconds) was found to compete with valeric acid. High Mn favors more valeric acid. On the other hand, low Mn gives more unknown 422. In the nonvolatile products, high Mn results in more glutaric acid while low Mn gives more glutaric semialdehyde. It is not clear how manganese affects the product patterns. An argument with dissolved oxygen goes to the wrong direction. In the presence of high Mn, the oxidation of calcium sulfite is oxygen mass transfer controlled, and the dissolved oxygen is practically zero. More oxygen would be required to produce glutaric acid than to produce glutaric semialdehyde from the decarboxylation product of adipic acid, RCH2•. Therefore, manganese must be able to carry oxygen to react with RCH2• to produce glutaric acid.

Table 5.7 Comparison of Organic Acids Buffer Additives

in Terms of k_{12} at pH 5.0, 55°C, in

Sodium Sulfite Solution by CO_2 Evolution

Organic Acid	Oxidative Degradation Rate Constant, $k_{12} \times 10^3$			
	$[S(IV)]_d$ (mM)	1 mM Mn	No Catalyst	0.1 mM Fe
Adipic	1.0	0.3	1.0	3.0
Glutaric	1.0	0.3	1.0	3.0
4-Hydroxybutyric	1.0	0.1	---	1.4
Hydroxyacetic	1.0	0.2	---	1.0
Malic	6.0	---	---	1.4
3-Hydroxybenzoic	2.0	0.3	---	-
2-Hydroxybenzoic	3.0	0.4	---	-
Benzoic	1.5	0.8	---	---
Sulfosuccinic	1.5	0.1	0.3	0.3
Maleic	5.0	3.6	6.7	7.0

Table 5.8 Rates of Sulfate Radical Reactions in Aqueous Solution

Reactant	Estimated $k(M^{-1}S^{-1})$	Literature $k(M^{-1}S^{-1})$	Reference
SO_3^{-2}	-	$\geq 5.3 \times 10^8$	Hayon et al., 1972
HSO_3^-	-	$>2.5 \times 5.3 \times 10^8$	"
Succinate	-	7.1×10^6	Maruthamuthu and Neta (1977)
fumarate	-	1.6×10^7	"
adipate	1.0×10^7	-	-
Fe^{2+}	8.6×10^8	9.9×10^8	Heckel et al., 1966
Mn^{2+}	1.8×10^{10}	-	-
Br^-	1.7×10^9	$(3.5 \pm 0.4) \times 10^9$	Redapath and Willson (1975)
Cl^-		1.3×10^8	Kim and Hamill, 1976
OH^-		4.6×10^7	Roebke et al., 1969
H_2O		10^3-10^4	Pennington and Haim, 1968
HSO_5^-		$<10^5$	Maruthamuthu and Neta, 1977

5.3 ALTERNATIVE ORGANIC ACIDS

The degradation behavior of several potential organic acid additives for wet scrubbing is summarized in Table 5.7. The organic acids covered here can be classified as dicarboxylic (adipic, glutaric), hydroxycarboxylic (hydroxyacetic, 4-hydroxybutyric, malic), sulfocarboxylic (sulfosuccinic), and unsaturated (maleic) acids.

The oxidative degradation rate constant, k_{12}, was a strong function of classification as shown in Table 5.7. Adipic and glutaric acids basically degrade at the same rate. The hydroxycaroxylic acids have significantly smaller k_{12} values. Simple monocarboxylic acids degrade at rates comparable to dibasic acids. Therefore, the smaller k_{12} of hydroxyacetic and 4-hydroxybutyric acids is not because of being monobasic when compared to the adipic and glutaric acids. Malic acid, a dibasic acid with a hydroxyl group, degrades significantly slower than adipic or glutaric acid in the presence of 0.1 mM Fe. The hydroxyl group reduces degradation, probably not through intramolecular hydrogen bonding.

Maleic acid degrades about seven times faster than saturated dicarboxylic acids, probably due to the presence of carbon-carbon double bonds. In reducing the degradation of maleic acid, Mn is not as effective as in the case of saturated dicarboxylic acids. Fe is inert to maleic acid degradation. On the other hand, the sulfonation product of maleic acid, i.e. sulfosuccinic acid, degrades much slower and behaves more or less in the same way as 4-hydroxybutyric acid except that Fe has no significant effect on the degradation of sulfosuccinic acid.

5.4 KINETIC MODEL

The degradation of organic acid under FGD conditions is found to be closely related to the oxidation of S(IV): (1) organic acid degradation is proportional to S(IV) oxidation; (2) degradation rate is proportional to the concentration of organic acid and inversely proportional to $[S(IV)]_d$. These observations are successfully explained by the kinetic model proposed by Rochelle (Section 2.2.1; Meserole et al., 1979). However, his model does not cover the effects of catalysts or inhibitors, which would be of more interest. Theoretically, if there is only one free radical responsible for both degradation and oxidation as implied by Rochelle's model, the oxidative degradation constant, k_{12}, should not be affected by changing catalyst environment. However, it is observed that:

(1) manganese reduces k_{12},
(2) iron increases k_{12},
(3) halides, especially bromide and iodide, reduce k_{12}.

Transition metals are of more interest because of the omnipresence of manganese and iron and because of their opposite effects. In addition, it is also observed that:

(1) The inhibiting effect of manganese is more pronounced with lower levels of dissolved S(IV).
(2) In the absence of manganese, dissolved S(IV) has a much weaker effect on k_{12}.
(3) The effects of both manganese and iron are bounded. With high levels of manganese, k_{12} is never less than 0.0001; with high levels of iron, k_{12} is never greater than 0.004.

A successful mechanism should be able to predict these trends and bounds.

5.4.1 MECHANISM

Figure 5.9 gives a mechanism proposed to rationalize the experimental observations. Any simplification of this mechanism will just result in worse correlation. This mechanism is based on the following assumptions:

$$SO_4^- + OA^- \xrightarrow{kd1} SO_4^{2-} + OA \tag{5.7}$$

$$Mn^{3+} + OA^- \xrightarrow{kd2} SO_4^{2-} + OA \tag{5.8}$$

$$OA \xrightarrow{kd0} \text{Degradation} \tag{5.9}$$

$$Fe^{2+} + HSO_5^- \xrightarrow{ki1} Fe^{3+} + SO_4^- \tag{5.10}$$

$$Fe^{3+} + SO_3^{2-} \xrightarrow{ki2} Fe^{2+} + SO_3^- \tag{5.11}$$

$$Mn^{3+} + SO_3^{2-} \xrightarrow{ki2'} Mn^{2+} + SO_3^- \tag{5.12}$$

$$SO_4^- + SO_3^{2-} \xrightarrow{ki3} SO_4^{2-} + SO_3^- \tag{5.13}$$

$$SO_4^- + Fe^{2+} \xrightarrow{ki4} SO_4^{2-} + Fe^{3+} \tag{5.14}$$

$$SO_4^- + Mn^{2+} \xrightarrow{ki4'} SO_4^{2-} + Mn^{3+} \tag{5.15}$$

$$SO_3^- + O_2 \xrightarrow{kp1} SO_5^- \tag{5.16}$$

$$SO_5^- + SO_3^{2-} \xrightarrow{kp2} SO_3^- + HSO_5^- \tag{5.17}$$

$$SO_5^- + SO_3^{2-} \xrightarrow{kp2'} SO_4^{2-} + SO_4^- \tag{5.18}$$

$$HSO_5^- + SO_3^{2-} \xrightarrow{kp3} 2\ SO_4^{2-} \tag{5.19}$$

$$2\ SO_3^- \xrightarrow{kt} \text{stable products} \tag{5.20}$$

Figure 5.9: A Mechanism for the Oxidative Degradation of Organic Acid Conjugated with Sulfite Oxidation

(1) Only sulfate radical (eq. 5.7) and manganic ion (eq. 5.8) react with organic acids to cause significant degradation of organic acids, primarily decarboxylation.

(2) Organic radical involved reactions except the degradation of organic acids are negligible.

The second assumptiom is made to simplifiy the mechanism. The first assumption will be dicussed in Section 5.4.2.1. The quantitative result of the proposed mechanism is a relationship for the oxidative degradation constant, k_{12}, which is calculated from experimental data by the following equation:

$$k_{12} = \frac{\text{degradation rate}}{\text{oxidation rate}} \times \frac{[\text{S(IV)}]\text{d}}{[\text{organic acid}]} \qquad (5.22)$$

Recognizing that sulfate radical (eq. 5.7) and manganic ion (eq. 5.8) react with organic acids at much slower rates than with S(IV) (eq. 5.13, 5.12) and assuming that intermediates reach steady state concentrations, equation 5.22 and the mechanism proposed above lead to an expression of the oxidative degradation constant, k_{12}, (eq. 5.23; Appendix E) with three variables: dissolved S(IV), manganese, and iron.

$$k_{12} = \frac{Kd1}{2ki3}\left(\frac{kp2'}{kp2 + kp2'} + \frac{\frac{kp2'}{kp2 + kp2'}}{1 + \frac{kp3}{kl1}\frac{[S(IV)]}{[Fe]}}\right)\frac{\left(1 + \frac{kd2}{kd1}\frac{k14'}{ki2'}\frac{[Mn]}{[S(IV)]}\right)}{\left(1 + \frac{ki4'}{ki3}\frac{[Mn]}{[S(IV)]} + \frac{ki4}{ki3}\frac{[Fe]}{[S(IV)]}\right)} \qquad (5.23)$$

Sixty six data points collected from sodium sulfite solution experiments were used for correlation. These data can be grouped as (1) no Mn/no Fe, (2) no Mn/Fe>0, (3) Mn>0/no Fe, and (4) Mn>0/Fe>0. A background concentration of iron (Fe0) is introduced because iron or a comparable catalyst must be present to initiate the reaction. Therefore, equation 5.23 ends up with seven adjustable parameters after replacement of [Fe] with [Fe + Fe0], where

[Fe] is the known amount of iron added to the reactor. The parameters were solved by using ZXMIN, an IMSL subroutine for nonlinear regression. The parameters obtained are listed below:

kd1/(2ki3) = 0.0041
kp2'/(kp2 + kp2') = 0.227
kp3/ki1 = 0.0184
(kd2/kd1)(ki4'/ki2') = 0.85
ki4'/ki3 = 11.93
ki4/ki3 = 0.65
[Fe0] = 0.0007 mM

The experimental and calculated values of k_{12} are compared in Figure 5.10.

The oxidative degradation constant, k_{12}, expressed by equation 5.23 implies the following features:

(1) With small concentrations of Mn and Fe, k_{12} approaches a constant value, (kd1/2ki3)×(kp2')/(kp2+kp2'), which is calculated to be 0.00093.

(2) As the ratio of manganese to dissolved S(IV) increases, the oxidative degradation constant, k_{12}, approaches a 'floor' value, 0.071, which is the multiplication of the corresponding k_{12} without Mn and the factor, (kd2/kd1)×(ki4'/ki2')/(ki4'/ki3).

(3) Iron tends to increase k_{12} because of (kp3/ki1)×[S(IV)]/[Fe] and tends to decrease k_{12} because of (ki4/ki3)×[Fe]/[S(IV)]. Therefore, the effect of iron on k_{12} will vanish over a certain range of iron concentration because of these two opposite effects.

(4) The effect of iron is upper bounded by a k_{12} value of 0.0041, equal to kd1/(2ki3).

(5) The effects of manganese and iron are more pronounced at low levels of dissolved S(IV).

5.4.2 DISCUSSION

5.4.2.1 Organic Acid Reactions.

Peroxydisulfates have been extensively studied for oxidizing organic compounds (Kennedy and Stock, 1960; Eibenberger et al., 1978) especially organic acids (Vasudeva and Wasif, 1972; Vasudeva, 1975; Srivastava et al., 1978). The sulfate radical anion is a well established intermediate in the thermal and photolytical decomposition of peroxydisulfates (Fronaeus and Ostman, 1968; Kolthoff and Miller, 1951; House, 1962). The sulfate radical is believed to be responsible for attacking organic compounds to cause degradation (eq. 5.7, Norman et al., 1970). The sulfate radical, SO_4^-, is a strong oxidant which can react with many organic and inorganic compounds by direct electron transfer oxidation. The reactions of this radical have been studied in some detail (Ross and Neta, 1979). Oxidative degradation of organic acids by Mn^{3+} has also been studied (eq. 5.8, Anderson and Kochi, 1970).

Additional evidence demonstrates that sulfate radical reacts with organic acid under FGD conditions:

(1) Sulfate radical can be easily derived from peroxymonosulfate, SO_5^{2-}, an expected intermediate, by analogy to peroxydisulfate, $S_2O_8^{2-}$.

(2) The correlated ratio of the reaction rates of sulfate radical with organic acid and with S(IV) is consistent with literature values as will be discussed in Section 5.4.2.1

(3) Previous work on oxidative degradation of organic acids indicates that decarboxylation is the major pathway (Vasudeva, 1975; Shukla, 1976; House, 1961), which is consistent with experimental observations (Table 5.5; Appendix D).

The hydroxyl radical is probably not responsible for organic acid degradation at FGD conditions. It is known to react with organic acids and can be generated from sulfate radical by reacting with water or hydroxyl ion (Table 5.8). However, at pH less than 8.5, these generation reactions are negligible (Norman et al., 1970). Although hydroxyl radical can also be derived from HSO_5^- by analogy to H_2O_2, the following three arguments make this radical less important under FGD conditions:

(1) The ratio of reaction rates of OH with organic acid and with S(IV) is probably much higher than as implied by experimental results. For instance, the reaction rate constant between OH and heptadicarboxylic acid is 2.4×10^9 $M^{-1}S^{-1}$ (Scholes and Willson, 1967) while the corresponding reaction rate constant for HSO_3^- is 2.1×10^9 $M^{-1}S^{-1}$ (Denisov,1972). These data will result in an oxidative degradation constant, k_{12}, hundred or even thousand times greater than as implied by experimental observations.

(2) The introduction of hydroxyl group into a dicarboxylic acid increases the rate of its oxidation by hydrogen peroxide (Walton and Graham, 1928), which is opposite to the observation under FGD conditions.

(3) The reaction of OH with carboxylate ions was shown to undergo decarboxylation only to a very limited extent (Garrison et al., 1953; Garrison et al., 1955), which is not consistent with the experimental observations under FGD conditions.

Therefore, it is very positive that it is sulfate radical not hydroxyl radical that participates in the oxidative degradation mechanism.

Ferric ion reacts with organic acids to cause degradation (Kuhnle et al., 1972) just like manganic ion does. It is impossible to include every reaction to get a reasonably simple mechanism. Fortunately, this simplification, by ignoring the aforementioned reaction, turns out to be not critical (Figure 5.10).

5.4.2.2 Sulfur Compounds Reactions

5.4.2.2.1 Sulfite Radical: A general form for the formation of sulfite radical, SO_3 , can be expressed by equation 5.24,

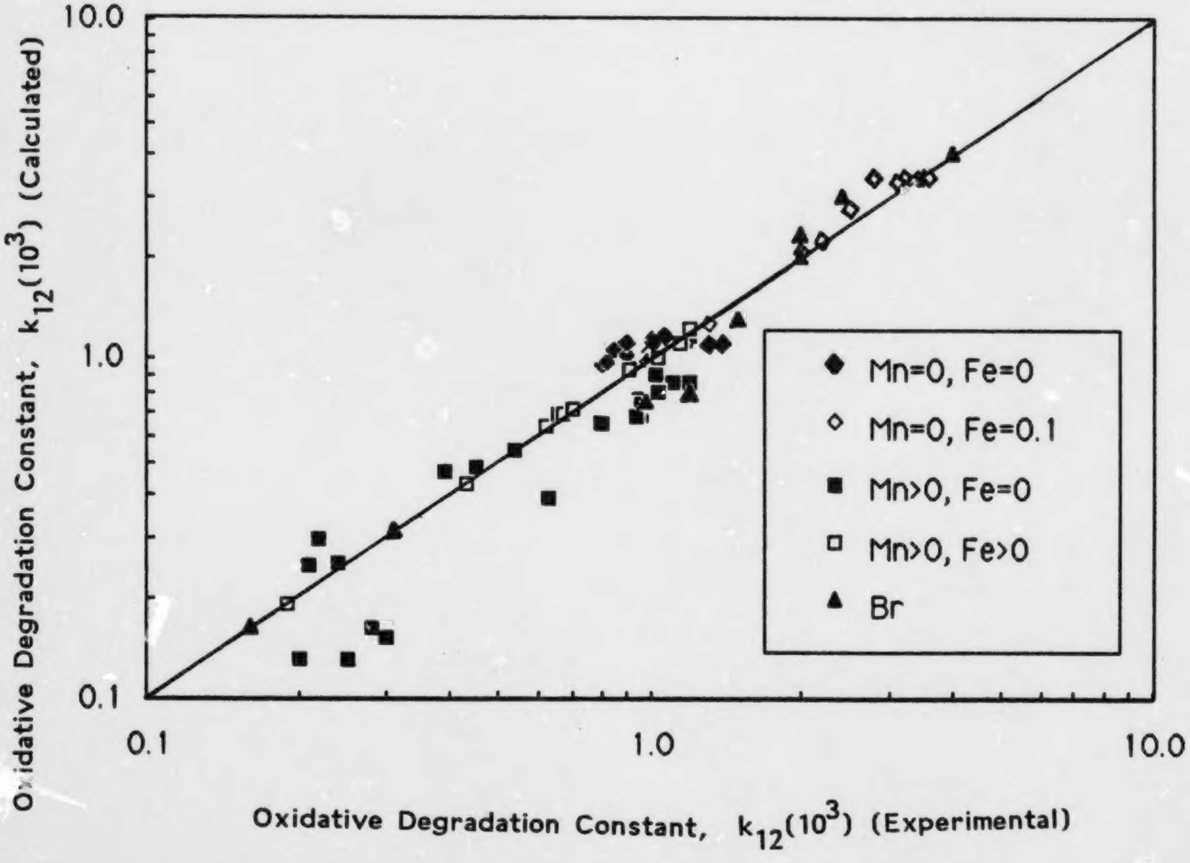

Figure 5.10: Comparison of Calculated and Experimental Values of k_{12}

$$R\bullet + SO_3^{2-} \dashrightarrow R^- + SO_3^- \qquad (5.24)$$

where R• is sulfate radical (SO_4^-, eq. 5.13), peroxymonosulfate radical (SO_5^-, eq. 5.17), ferric ion (Fe^{3+}, eq. 5.11), or manganic (Mn^{3+}, eq. 5.12). These reactions will be discussed later in appropriate sections.

The reaction of sulfite radical with O_2 (eq. 5.16) provides a way to 'activate' oxygen for the oxidation of S(IV). This reaction was also adopted by Backstrom (1934) and Hayon et al. (1972). The sulfite radical is not very reactive toward organic compounds. The reaction of sulfite radical with 1-propanol has a reaction rate constant as low as 2×10^3 $M^{-1}S^{-1}$ (Table 5.8; Hayon et al., 1972). However, the sulfite radical reacts with oxygen at a much higher rate, $<10^9$ $M^{-1}S^{-1}$ (Table 5.8; Hayon et al., 1972). In addition, sulfite radical reacts with itself at even a greater rate (Ross and Neta, 1979). This reaction is probably the major termination reaction under mass transfer controlled condition and is also one of the termination reactions proposed by Backstrom (1934). The stable termination products were reported to be sulfur trioxide, which will be hydrolyzed to sulfate, sulfite, and dithionate (Ross and Neta, 1979).

5.4.2.2.2 Sulfate Radical: The sulfate radical is a very reactive one electron transfer oxidizing agent. The reactions of sulfate radical with organic acid, ferrous ion, and manganous ion are discussed in appropriate sections. The reaction rate constants of some oxidative degradation related reactions, derived from correlation, are compared to literature values in Table 5.8.

The reaction of sulfate radical with HSO_3 is believed to be at least 2.5 times faster than with SO_3^{2-} (Ross and Neta, 1979). Therefore, the sulfate radical will react with S(IV) faster at lower pH. In contrast, the sulfate radical reacts with organic acid slower at lower pH. For instances, the reaction rate constants of SO_4^- with acetate and acetic acid are 5.6×10^6 (Table 5.8; Chawla and Fessender, 1975) and $(8.8\pm0.2)\times10^4$ (Table 5.8; Dogliotti and Hayon, 1968) respectively. Therefore, smaller oxidative degradation constant, k_{12}, is expected at lower pH. However, this effect of pH was not observed over the pH range 4 - 6.

At high pH, more sulfate radical will be consumed by reacting with hydroxyl ion. However, the reaction rate constant, 4.6×10^{7} $M^{-1}S^{-1}$ (Roebke et al., 1969) is not high enough to have significant effect at pH 4 to 6, where the concentration of hydroxyl ion is very low compared to the concentration of S(IV) or organic acid. Probably the most important reason is that HSO_3 still dominates when pH changes from 4 to 6, because of the high pKa value, 7.2 (Yui, 1940). However, the pKa values of adipic acid, 4.4 and 5.4 (Serjeant and Dempsey, 1979; Gane and Ingold, 1931) are in the scope covered by the studied pH range, pH 4 to 6. It is still not clear about the absence of the effect of pH on the oxidative degradation constant, k_{12}.

5.4.2.2.3 Peroxymonosulfate: The peroxymonosulfate radical, SO_5^-, is logically derived from the reaction of sulfite radical with oxygen (eq. 5.16). The peroxymonosulfate radical thus formed reacts with S(IV) to produce sulfate radical, sulfite radical, and peroxymonosulfate, SO_5^{2-}, in parallel reactions (eq. 5.17, 5.18). The formation of SO_3^- and SO_5^- (eq. 5.17) was favored by Backstrom (1934) while the formation of SO_4^- (eq. 5.18) was favored by Hayon et al., (1972). The coexistence of these two reactions suggests a minimum k_{12} corresponding to the fraction of peroxymonosulfate radical, SO_5^-, that reacts with S(IV) to form sulfate radical. According to the correlation results, the minimum k_{12} for Mn and Br systems would be 0.7×10^{-4} and 0.2×10^{-3} respectively. The parallel reactions are expected to generate more sulfite radical and peroxymonsulfate than sulfate radical because of direct electron transfer. This prediction agrees with the correlation result which suggests four times faster reaction rate for the former reaction.

Refering to the oxidative degradation constant (k_{12}) expression (eq. 5.23), it is clear that the direct production of SO_4^- from SO_5^- (eq. 5.18) is not affected by iron while the indirect production of SO_4^- from SO_5^- (eq. 5.10) through the formation of SO_5^{2-} intermediate (eq. 5.17) is catalyzed by iron. Therefore, SO_5^- is the precursor of SO_4^-, which is the major species responsible for the degradation of organic acid. Since the formation of SO_5^- is inevitable, the degradation of organic acid in conjugation with S(IV) oxidation is also inevitable.

In the absence of manganese or comparable inhibitor, the minimum k_{12} occurs at infinitely dilute iron and is estimated to be 0.0009. However, the proposed mechanism needs iron to initiate the chain reaction. Based on the correlation results, the background level iron concentration is around 0.0007 mM, which is very close to the measured iron concentration, 0.0005 mM in 0.3 M sodium sulfate solution (Owens, 1984). The application of 0.3 M sodium sulfate solution is to avoid dramatic change in sulfate concentration or ionic strength during the progress of S(IV) oxidation.

The reaction of peroxymonosulfate ion with ferrous ion (eq. 5.10) is assumed to be the primary initiation reaction and is discussed in Section 5.4.2.3. Peroxymonosulfate may also oxidize S(IV) to S(VI) directly (eq. 5.19) as suggested by Backstrom (1934). Refering to k_{12} expression equation (eq. 5.23), the incorporation of this reaction in the mechanism is necessary to match the experimental observation that iron increases k_{12}.

5.4.2.3 Iron Reactions

The reaction of ferrous with peroxymonosulfate to produce ferric and sulfate radical (eq. 5.10) is the primary initiation reaction. It is well known that ferrous ion reacts with peroxides to form ferric and a free radical formed by splitting the peroxide bond (Kolthoff and Medalia, 1949; Kothoff et al., 1951). Because of the argument made in Section 5.4.2.1, the free radical is thought to be sulfate radical instead of hydroxyl radical. This reaction (eq. 5.10) was also suggested by Huie (1985) and by Rochelle et al. (1985).

Ferrous ion reacts with sulfate radical (eq. 5.14) at a significant rate (Table 5.8; Heckel et al., 1966). Therefore, iron generates sulfate radical (eq. 5.10) to increase organic acid degradation on one hand and deplete sulfate radical (eq. 5.14) to decrease the degradation on the other hand. Ferrous ion is oxidized to ferric ion in both equations 5.10 and 5.14. The reaction of ferric ion and S(IV) (eq. 5.11) provides a logical route for ferrous regeneration. The ratio of the reaction rate of SO_4^- with Fe^{2+} to that with S(IV), ki4/ki3, is estimated to be <0.75 (Table 5.8; Heckel et al., 1966; Ross and Neta, 1979), which is in good agreement with the correlation result, 0.65.

The kinetic chain length can be defined as the ratio of propagation (eq. 5.16) rate and initiation rate (eq. 5.10). The chain length is derived to be :

$$\text{Chain length} = 1.3 + 0.24 \times [S(IV)]/[Fe] \qquad (5.25)$$

Equation 5.25 predicts a minimum chain length of 1.3. In addition, it also predicts that the chain length would be shortened by adding iron, which is experimentally observed by Ulrich (1983), and would be elongated by increasing dissolved S(IV).

5.4.2.4 Manganese Reactions

When manganese compounds are employed in a catalytic capacity, the metal species is thought to alternate between II and III oxidation states. Manganic ion reacts with organic acids to cause degradation (eq. 5.8; Anderson and Kochi, 1970). To provide a route for manganous regeneration, manganic ion should also react with S(IV) (eq. 5.12) by analogy to the reaction between ferric ion and S(IV) (eq. 5.11). The ratio of the reaction rate of Mn^3 with organic acid to that with S(IV), kd2/ki2', is 0.0006, an order of magnitude smaller than the sulfate radical counterpart, kd1/ki3 (0.0082). In other words, in terms of oxidative degradation of organic acid, manganic ion is less important than sulfate radical.

By analogy to the reaction between ferrous ion and sulfate radical (eq. 5.14), manganous ion reacts with sulfate radical (eq. 5.15). The latter reaction is necessary for the mechanism to match the observation that manganese decreases k_{12}. The reaction rate constant is estimated to be 1.8×10^{10} from the reaction rate constant of the ferrous counterpart and the ratio ki4'/ki4, which is correlated to be 18.4. Accordingly, sulfate radical should react with manganous faster than with ferrous by an order of magnitude.

5.4.2.5 Halide Reactions

It is believed that the reason why manganese decreases the oxidative degradation constant, k_{12}, is because of the fast reaction between Mn^{2+} and SO_4^- (eq. 5.15). The reaction rate constant is estimated in Section 5.4.2.4 to be 1.8×10^{10}. Similarly, halides inhibit organic acid degradation via the same mechanism. The corresponding constants of bromide and chloride are 3.5×10^9 (Redapath and Willson, 1975) and 1.3×10^8 (Kim and Hamill, 1976) respectively. Therefore, in reducing the oxidative degradation constant, k_{12}, Mn^{2+} would be an order of magnitude more powerful than Br^-, and Br^- would be more powerful than Cl^- by another order of magnitude. These predictions are consistent with the experimental results. If bromide is used instead of manganese, the following equations should be included to replace the corresponding manganese equations 5.8, 5.15, and 5.12:

$$Br + OA^- \xrightarrow{kd(Br)} Br^- + OA \qquad (5.26)$$

$$Br^- + SO_4^- \xrightarrow{ki4(Br)} Br + SO_4^{2-} \qquad (5.27)$$

$$Br + SO_3^{2-} \xrightarrow{ki2(Br)} Br^- + SO_3^- \qquad (5.28)$$

Fixing the values of the remaining parameters as obtained earlier from manganese system, the correlation results lead to estimations of the following ratios of reaction rate constants:

$$\frac{kd(Br)}{ki2(Br)} = 0.0002$$

$$\frac{ki4(Br)}{ki3} = 1.26$$

The experimental and calculated values of k_{12} are compared in Figure 5.10.

Compared to the SO_4^- counterpart value of kdl/ki3 (0.0082), the value of kd(Br)/ki2(Br) (0.0002) implies that bromide radical is less important than sulfate radical in contributing to the oxidative degradation of organic acids. The value of ki4(Br)/ki3 (1.26) gives 1.7×10^9 as the reaction rate constant between SO_4^- and Br^-, reported in the literature to be $(3.5\pm0.4)\times10^9$ (Redapath and Willson, 1975).

Not enough iodide data are available for the prediction of the reaction rate constant between iodide and sulfate radical. However, halide radicals tend to react with organic compounds in the decreasing order: $Cl_2^- > Br_2^- > I_2^-$ while halides tend to react with SO_4^- in the increasing order: $Cl^- < Br^- < I^-$ (Table 5.8; Ross and Neta, 1979). Therefore, iodide would inhibit organic acid degradation most efficiently while chloride would be the least efficient inhibitor. These trends are expected because of their relative strength in standard electrode potentials.

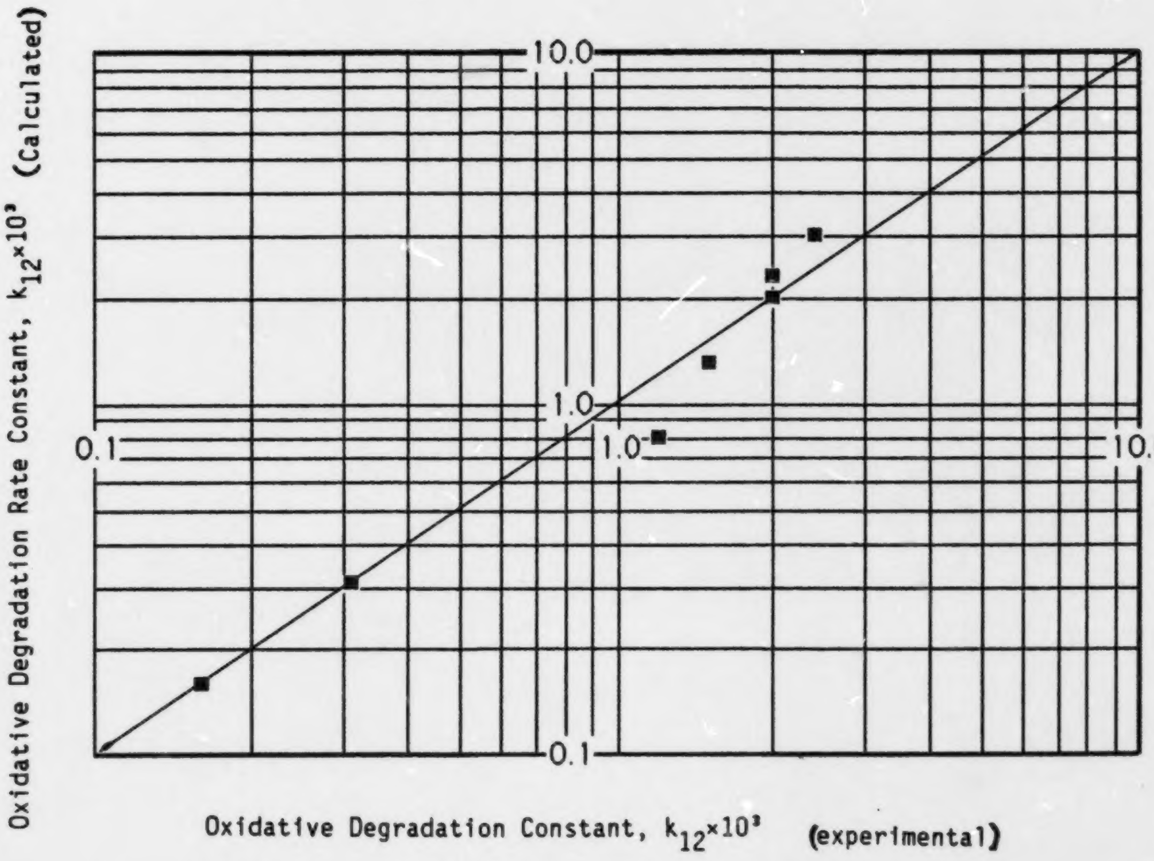

Figure 5.11: Comparison of Calculated and Experimental Value of k_{12}: Fe/Br System

SECTION 6 DESIGN AND OPERATING IMPLICATIONS

There are three important losses of soluble buffers: (1) entrained solution, (2) coprecipitation, and (3) oxidative degradation. The contribution of each loss is a strong function of operating conditions. Several cases are compared in this section. The analyses are based on the results of this study and on the results from previous industrial studies. These industrial results are available in Rochelle's (1982) review paper and are summarized as :

1. For natural oxidation, the oxidation level of absorbed sulfur dioxide depends on operating pH. The level is 50% for pH 4.5, 35% for pH 5.0, and 15% for pH 5.5.
2. Limestone utilization is increased at lower pH. The utilization is 80% for pH 5.5, 95% for pH 5.0, and 99% for pH 4.5.
3. Dewatering of waste solids is a strong function of percent oxidation. Complete oxidation gives waste with highest concentration of solids (85% W/W), while 20% natural oxidation gives only 50% solids.
4. The concentration of organic acid buffer required to achieve 90% SO_2 removal depends on its pKa value(s). For a specific organic acid, this concentration also depends on the oxidation level and operating pH. More organic acid is required at low pH with natural oxidation; while at high pH with forced oxidation, the organic acid concentration needed is significantly reduced. The values used in Table 6.1 are based on an L/G ratio of 100 gal/1000 ft^3.
5. The coprecipitation of organic acid with calcium sulfite solids is a function of oxidation level but not significantly affected by operating pH.

6.1 NATURAL VERSUS FORCED OXIDATION

Table 6.1 shows that organic acid consumption is reduced with forced oxidation at pH 4.5 (cases 1, 2), pH 5.0 (cases 3, 4), and pH 5.5 (cases 5, 6). As compared with natural oxidation, forced oxidation results in more degradation but gives drier waste solids and less loss by coprecipitation. The loss by coprecipitation is negligible for complete oxidation. On the other hand, oxidative degradation is a less significant loss for natural oxidation, where the losses by entrained solution and coprecipitation dominate.

Pilot plant data (Burbank and Wang, 1981) have shown that forced oxidation in general gives a high concentration of manganese, which is effective in reducing degradation. The data also show that dissolved iron, which increases the degradation of organic acid, is increased by high dissolved S(IV). Therefore, forced oxidation will not cause a very high loss by degradation at low dissolved S(IV) and natural oxidation will not result in zero degradation at high dissolved S(IV).

6.2 PH

Table 6.1 shows that high pH (5.5) requires less organic acid makeup than low pH (4.5) for both natural (cases 1, 5) and forced oxidation (cases 2, 6). The primary reason is that much less organic acid is required at high pH to achieve a certain performance (eg. 90% SO_2 removal) than at low pH. The effect of pH is more significant with natural oxidation where solution loss dominates. Although chemical degradation and coprecipitation increase as pH increases, they are compensated for by the reduction of the loss in the entrained solution.

6.3 THIOSULFATE

Thiosulfate is effective in inhibiting the oxidation of S(IV), but degrades very fast in the presence of sulfite oxidation. Table 6.1 shows that the addition of thiosulfate (case 13) is not very attractive from the viewpoint of operating cost. The addition of thiosulfate results in about 50% increase in total makeup cost when compared with forced oxidation at pH 5.5 (case 6, Table 6.1). However, the addition of thiosulfate also gives other benefits. It prevents scale formation and enhances solids dewatering (Rochelle, et al., 1985).

6.4 HALIDES

Halides, especially bromides and iodides, can significantly reduce organic acid degradation. Both bromide (case 15) and iodide (case 14) are attractive as additional additives, because the major loss of organic acid is by degradation with forced oxidation, and halides reduce oxidative degradation. In addition, small losses through entrained solution minimize the makeup cost of halides. The application of these halides as additives is still economical even when the weight percentage of waste solids is as low as 50%.

6.5 ALTERNATIVES

Hydroxy and sulfosuccinic acids degrade slower than adipic acid. Hydroxy acids inhibit the oxidation of S(IV) and consequently make degradation even less significant.

However, with natural oxidation these alternatives (cases 7, 9, 11) are not superior to DBA. With natural oxidation degradation is not the major loss. The most important loss is through entrained solution. Therefore there is no advantage in using these alternatives with natural oxidation. With forced oxidation where degradation dominates, these alternatives seem attractive, especially β-hydroxypropionic acid (case 10) and sulfosuccinic acid (case 12). The application of glycolic acid (case 8) is limited by its high concentration requirement.

Since β-hydroxypropionic and sulfosuccinic acids are not commercially available, they are assumed to have the same price as their precursors acrylic and maleic acids, respectively. It is known that maleic acid degrades at a rate about an order of magnitude faster than adipic acid. Acrylic acid may behave similarly because of the similarity of the molecular structure, i.e. the presence of a C=C double bond conjugated with the carboxyl group.

Table 6.1 The Effects of Operating Parameters on the Makeup Rate of Organic Acid Buffer for 90% SO2 Removal

Case	1	2	3	4	5	6
pH	4.5	4.5	5.0	5.0	5.5	5.5
Oxidation level (%)	50	100	35	100	15	100
Waste (wt% solids)	60	85	55	85	50	85
CaCO3 utilization (%)	99	99	95	95	80	80
Dissolved S(IV) (mM)	10	1	5	0.8	2	0.5
Organic acid	DBA[a]	DBA	DBA	DBA	DBA	DBA
unit price[b]($/Kg mole)	95.0[c]	95.0	95.0	95.0	95.0	95.0
conc.(mM)	23.0	10.0	15.0	7.5	6.8	4.3
ppm solid/ppm soln	0.5	0	0.8	0	1.5	0
$k_{12}(\times10^3)$	1.5	0.3	1.5	0.3	1.5	0.3
loss (mmole/gmole SO_2)						
-entrained soln	2.32	0.31	1.83	0.23	1.09	0.15
-coprecipitation	1.74	--	1.79	--	1.64	--
-degradation	1.73	3.00	1.57	2.85	0.77	2.58
Total makeup cost						
$/tonne $CaCO_3$	5.45	3.11	4.70	2.78	2.66	2.07
$/Kg mole SO_2	0.61	0.35	0.55	0.33	0.37	0.29
$/tonne SO_2	9.53	5.47	8.59	5.16	5.78	4.53

[a] dibasic acid.
[b] prices from Chemical Marketing Report (June 10, 1985)
[c] The price is estimated to be half of adipic acid

Table 6.1 The Effects of Operating Parameters on the Makeup Rate of Organic Acid Buffer for 90% SO2 Removal (contd.)

Case	7	8	9	10	11	12
pH	5.5	5.5	5.5	5.5	5.5	5.5
Oxidation level (%)	15	100	15	100	15	100
Waste (wt% solids)	50	85	50	85	50	85
CaCO3 utilization (%)	80	80	80	80	80	80
Dissolved S(IV) (mM)	3	0.8	3	0.8	2	0.8
Organic acid	glycolic		β-hydroxy propionic		sulfosuccinic	
unit price ($/Kg mole)	82.9	82.9	98.4[d]	98.4	75.4[e]	75.4
conc.(mM)	18.4	11.6	11.3	7.2	9.4	6.0
ppm solid/ppm soln	1.5	0	1.5	0	1.5	0
$k_{12}(\times 10^3)$	0.3	0.2	0.3	0.2	0.2	0.1
loss (mmole/gmole SO_2)						
-entrained soln	2.95	0.40	1.81	0.25	1.51	0.21
-coprecipitation	4.43	--	2.72	--	2.26	--
-degradation	0.28	2.90	0.17	1.79	0.14	0.77
Total makeup cost						
__$/tonne CaCO3	5.08	2.19	3.70	1.61	2.36	0.60
__$/Kg mole SO_2	0.71	0.30	0.51	0.22	0.33	0.08
__$/tonne SO_2	11.1	4.69	7.97	3.44	5.16	1.25

[d] the price is estimated from acrylic acid

[e] the price is estimated from maleic waste acid

Table 6.1 The Effects of Operating Parameters on the Makeup Rate of Organic Acid Buffer for 90% SO2 Removal (contd)

Case	13	14	15
pH	5.5	5.5	5.5
Oxidation level (%)	2	100	100
Waste (wt% solids)	70	85	85
CaCO3 utilization (%)	80	80	80
Dissolved S(IV) (mM)	2	0.8	0.8
Organic acid	DBA	DBA	DBA
unit price ($/Kg mole)	95.0	95.0	95.0
conc.(mM)	6.8	4.3	4.3
ppm solid/ppm soln	2.5	0	0
$k_{12}(\times 10^3)$	1.0	0.1	0.2
loss (mmole/gmole SO_2)			
-entrained soln	0.45	0.15	0.15
-coprecipitation	2.63	--	--
-degradation	0.07	0.54	1.08
-makeup cost($/tonne $CaCO_3$)	8.11	1.76	3.15
other additive	$Na_2S_2O_3$	I(KI)	$Br(Br_2)$
conc.(mM)	1.5	0.1	10
unit price ($/Kg mole)	156.5[f]	3923	232.5
-makeup cost($/tonne $CaCO_3$)	0.80	0.11	0.08
Total makeup cost			
$/tonne CaCO3	3.24	0.63	1.00
$/Kg mole SO_2	0.45	0.09	0.14
$/tonne SO_2	7.03	1.41	2.19

f Rochelle et al., 1985

SECTION 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

1. The degradation of organic acid is conjugated with sulfite oxidation and can be expressed kinetically in terms of the 'oxidative degradation constant', k_{12}, which is defined as:

$$k_{12} = \frac{\text{organic acid degradation rate}}{\text{sulfite oxidation rate}} \times \frac{\text{dissolved S(IV) conc.}}{\text{organic acid conc.}}$$

The oxidative degradation constant, k_{12}, is independent of oxygen mass transfer conditions, organic acid concentration, and pH.

2. The proposed free radical mechanism correlates the experimental k_{12} from 0.0001 to 0.0036 within 30% for 0.3 - 10 mM S(IV), 0 - 0.1 mM Fe, 0 - 1.2 mM Mn, and 0 - 10 mM Br.
3. Sulfate radical is the primary free radical responsible for the oxidative degradation of organic acids.
4. Iron competes with dissolved S(IV) for peroxymonosulfate to produce sulfate radical and hence increases k_{12} from 0.001 to 0.0036 when iron concentration increases from background level (0.0007 mM) to 0.1 mM. No k_{12} greater than 0.004 has been observed.
5. Manganese competes with dissolved S(IV) for depleting sulfate radical and hence decreases k_{12} from 0.001 to 0.0002 when manganese concentration increases from zero to 1.0 mM. In addition to sulfate radical, manganic ion also causes the degradation of organic acids. Therefore, the effect of manganese is bounded and no k_{12} less than 0.0001 has been observed.
6. Halides resemble manganese in reducing k_{12}. With 1 mM dissolved S(IV), 0.1 mM manganese gives effects comparable to <0.1 mM iodide, 1 mM bromide, or 100 mM chloride.

7. Lower dissolved S(IV) magnifies the catalytic and inhibiting effects of iron, manganese, and halides.
8. Thiosulfate inhibits sulfite oxidation and consequently stops organic acid degradation. In the presence of manganese, thiosulfate decreases k_{12} at low levels of dissolved S(IV).
9. Among other transition metals, cobalt and nickel increase k_{12} an order of magnitude less efficiently than iron while thallium appears to reduce k_{12} and titanium, vanadium, chromium and copper have no significant effects.
10. Decarboxylation is the major degradation pathway. With 0.03 mM manganese, 1.3 mole carbon dioxide is generated from every mole of glutaric acid degradation up to 30% conversion. At high conversion (80%), as much as 49% of the carbon of adipic acid is degraded to carbon dioxide.
11. With 0.1 mM manganese at 80% conversion, The other degradation products of adipic acid are smaller dicarboxylic acids (4%), monocarboxylic acids (3%), hydroxycarboxylic acids (5%), hydrocarbons (1%), glutaric semialdehyde (7%), and other carbonyl compounds (1%).
12. In the presence of high manganese (1.0 mM), the retained degradation products of adipic acid are primarily valeric acid and glutaric acid. With a low concentration of manganese (<0.1 mM), the degradation products are significantly different and include significant quantities of glutaric semialdehyde.
13. Hydroxyacids and sulfonated acids degrade slower than simple dicarboxylic acids by a factor of three while maleic acid, an unsaturated dicarboxylic acid, degrades faster than simple dicarboxylic acids by a factor of seven. Therefore, hydroxyacids and aldehydeacids, which are sulfonated under FGD conditions, tend to accumulate as ultimate liquid phase degradation products.

7.2 RECOMMENDATIONS

1. The oxidation of S(IV) under FGD conditions should be studied further with emphasis on the individual and combined effects of manganese, iron, halides, and free radical scavengers to better understand the mechanism. Dissolved S(IV) and oxygen should be monitored during the experiments to confirm the effects of these two variables.
2. Organic acids and their deliberate derivatives should be studied for oxidative degradation to differentiate electron transfer mechanism and hydrogen abstraction. Decarboxylation and general degradation can then be discriminated and compared as a function of functional group composition and catalyst environment.
3. The degradation product distribution should be studied as a function of reaction time or conversion to understand better the oxidative degradation of organic acids.
4. The oxidative degradation experiments should be conducted over a broad pH range, 3 to 7, to observe the effect of pH on the degradation of organic acids.
5. Thiosulfate and halides, especially iodide and bromide should be tested in combination with organic acids in FGD scrubbing systems on a pilot plant scale to investigate possible beneficial effects. If oxidation is inhibited, then unsaturated acids such as maleic acid would have makeup rates comparable to DBA or adipic acid.
6. If high level of sulfite oxidation is expected, formic acid and maleic acid are inferior to other alteratives such as DBA and adipic acid.

APPENDICES

Appendix A Experimental Data

Table XA.1 Detailed Data of Slurry Experiments in Open System

Time (hr)	pH	Temp (°C)	H2SO4 5_N(ml)	$[S(IV)]_t$ _(M)_	Adipic (mM)	
Run # AA1						
0	5.5	52.0		1.64	9.2	
1	5.5	65.5		1.29	7.8	
1.75	5.5	66.8		1.09	6.5	
2.25	5.5	68.0		0.85	4.8	
2.75	5.5	72.8	3.70	0.58	4.3	
3.25	5.5	81.0		0.18	3.7	
Run # AA2						
						Glycolic(mM)
0	5.5	53.0	0	1.67	9.7	11.4
0.75	5.5	64.0	0.96	1.45	8.6	11.4
1.50	5.5	67.5	2.05	1.34	8.4	11.8
2.25	5.5	65.0	3.24	1.18	7.5	11.0
3.00	5.5	63.0	4.85	0.95	7.0	10.9
4.25	5.5	74.0	8.54	0.21	4.5	8.4
4.50	4.4	71.5	8.91	0.07	4.2	8.5
Run # AA3 (10 mM Glycolic)						
0	4.5	48.0	0	1.97	9.4	
0.75	4.5	61.6	0.03	1.58	9.3	
1.50	4.5	66.0	0.03	1.23	9.2	
2.25	4.5	68.0	0.03	0.72	9.0	
3.00	4.5	68.0	0.53	0.35	8.6	
3.75	4.5	73.0	0.87	-	8.5	
Run # AA4 (1 mM sodium thiosulfate)						
0	4.5	45.0	0	1.72	10.7	
1.50	4.5	50.1	0	1.72	10.9	
3.00	4.5	53.0	0	1.70	10.8	
Run # AA5 (1 mM sodium thiosulfate, 1 mM Mn)						
0	4.5	53.0		1.70	10.7	
1.00	4.5	67.6		1.27	10.2	
2.00	4.5	67.6		0.87	9.7	
3.00	4.4	78.6		0.05	9.4	
3.50	3.2	68.5		-	9.2	
Run # AA6 (0.3 M magnisium sulfate, 1 mM sodium thiosulfate)						
0	5.0	51.5	0	0.73	10.0	
0.5	4.9	64.2	0.12	0.55	9.8	
1.00	4.7	70.4	0.12	0.19	9.7	
1.50	4.6	72.2	0.12	-	9.2	
Run # AA7 (0.3 M magnesium sulfate, 10 mM sodium sulfate)						
0	5.0	50.6	0	0.77	9.9	
2.00	5.0	53.2	0.55	0.75	9.9	
6.67	4.9	54.0	0.55	0.67	10.1	
Run#AA8(0.3 M magnesium sulfate,10 mM sodium thiosulfate,0.3 mM Mn)						
0	5.0	54.0	0	0.67	10.1	
0.50	4.7	65.2	0	0.44	9.3	
1.00	3.2	58.0	0	-	9.1	
Run # AA9 (10 mM sodium thiosulfate, 1 mM Mn)						
0	5.5	53.0	0	1.01	10.0	
1.00	5.5	53.0	0	1.00	10.0	
Run # AA10 (10 mM sodium thiosulfate, 1 mM Mn)						
0	5.0	52.0	0	1.00	10.0	
1.00	5.0	52.0	0	1.00	10.0	

Time (hr)	pH	Temp (°C)	H2SO4 5_N(ml)	$[S(IV)]_t$ _(M)_	Adipic (mM)
Run # AA11 (10 mM sodium thiosulfate, 1 mM Mn)					
0	4.5	51.0	0	0.99	10.0
1.00	4.5	52.0	0.64	1.05	10.0
2.00	4.5	52.0	1.08	0.99	10.0
2.50	4.5	52.0	1.16	1.00	10.0
Run # AA12 (1 mM sodium thiosulfate)					
0	5.5	44.0	0	1.04	10.5
1.00	5.5	51.0	0	0.96	10.0
2.00	5.5	54.0	0	0.89	10.0
Run # AA13 (1 mM sodium thiosulfate, 1 mM Mn)					
0	5.5	54.0	0	0.89	10.0
0.50	5.5	64.0	0	0.64	10.0
1.25	5.5	73.0	0.13	0.17	8.4
1.67	5.0	68.0	0.20	0.02	7.1
Run # AA14 (3 mM sodium thiosulfate, 1 mM Mn)					
0	5.5	49.4		0.94	10.1
0.50	5.5	51.7		0.94	10.0
1.50	5.5	52.8		0.94	10.0
2.50	5.5	52.8		0.94	9.9
Run # AA15 (3 mM sodium thiosulfate, 1 mM)					
0	5.0	51.7		0.94	9.9
0.75	5.0	51.7		0.94	9.3
Run # AA16 (3 mM sodium thiosulfate, 1 mM Mn)					
0	4.5	51.1		0.94	9.3
0.83	4.5	58.3		0.84	9.0
2.08	4.1	74.4		0.03	8.4
Run # AA17 (2 mM sodium thiosulfate, 1 mM Mn)					
0	5.5	45.6		0.98	10.0
1.00	5.5	51.7		0.97	9.8
2.67	5.5	53.3		0.97	10.1
3.50	5.5	53.3		0.96	10.0
Run # AA18 (2 mM sodium thiosulfate, 1 mM Mn)					
0	5.0	53.3		0.96	10.0
0.50	5.0	62.8		0.69	9.5
1.00	5.0	70.0		0.44	9.1
1.50	4.9	73.9		0.13	9.3
2.00	4.4	66.7		0.05	8.9
Run # AA19 (1.2 mM sodium thiosulfate, 1 mM Mn)					
0	5.5	45.6	0	0.95	10.7
0.50	5.5	60.6	0.52	0.75	11.0
1.00	5.5	67.8	0.52	0.50	9.6
1.50	5.5	72.8	0.52	0.29	9.6
2.17	5.5	71.1	0.52	0.05	8.8
4.00	5.2	55.6	0.52	-	8.8
Run # AA20 (0.5 mM sodium thiosulfate, 1 mM Mn)					
0	5.5	51.1	0	0.88	10.3
0.58	5.5	62.8	0.23	0.64	10.0
0.92	5.5	66.7	0.38	0.47	8.8
1.33	5.5	71.7	0.57	0.23	8.4
1.67	5.4	73.9	0.64	0.06	8.1
3.00	4.8	55.0	0.64	-	8.0

Time (hr)	pH	Temp (°C)	H_2SO_4 5 N(ml)	$[S(IV)]_t$ (M)	Adipic (mM)	a	b
Run # AA21 (0.1 mM Mn)							
0	5.5	55.6	0	1.20	6.8	1.8	0.8
0.83	5.5	62.8	2.39	0.96	4.6	1.4	0.8
1.67	5.5	62.2	4.71	0.69	2.8	1.2	0.5
2.50	5.5	58.3	5.83	0.56	1.8	0.7	0.3
3.33	5.5	56.1	6.30	0.49	2.0	0.5	0.5
4.17	5.5	55.0	6.66	0.44	1.4	0.6	0.3
14.5	5.5	53.3	8.63	0.18	1.4	0.5	0.8

a. glutaric; b.succinic

Run # AA22 (3 mM Mn)					
0	5.5	52.2	0	0.81	9.8
0.33	5.5	59.4	0.45	0.64	10.4
0.67	5.5	64.4	1.11	0.51	10.4
1.00	5.5	67.2	1.30	0.35	10.0
1.33	5.5	68.9	1.66	0.18	10.0
1.67	5.5	70.0	1.96	0.03	9.6
Run # AA23 (3 mM Mn)					
0	5.5	56.7	0	0.68	9.1
0.33	5.5	62.2	0.24	0.56	8.1
0.67	5.5	67.2	0.52	0.40	8.1
1.00	5.5	70.0	0.92	0.23	7.2
1.33	5.5	71.1	1.29	0.07	5.6
1.50	4.9	68.3	1.33	-	5.2
Run # AA24 (0.1 mM Mn)					
0	5.5	46.1	0	1.11	50.0
0.50	5.5	54.4	0.38	0.96	
1.00	5.5	61.1	0.98	0.79	
1.50	5.5	62.2	1.57	0.60	
2.00	5.5	65.0	2.08	0.45	
2.50	5.5	63.3	2.58	0.35	
3.00	5.5	62.2	2.92	0.30	
3.50	5.5	60.6	3.22	0.22	
4.17	5.5	58.9	3.57	0.13	40.0
					Glutaric
Run # G1					
0	4.6	55.0		0.82	9.8
0.16	4.6			0.80	9.7
0.33	4.6			0.75	9.2
0.58	4.6			0.66	9.5
1.00	4.6			0.52	9.0
Run # G2 (1 mM Mn)					
0	5.5	46.1	0	0.95	9.7
0.58	5.5	57.8	0.63	0.74	10
1.00	5.5	60.8	1.16	0.60	9.7
1.50	5.5	65.6	1.75	0.45	9.0
2.00	5.5	71.1	2.48	0.14	8.5
2.67	4.4	55.0	2.51	-	7.5
Run # G3					
0	5.5	50.9	0	1.47	9.1
5.00	5.5	52.8	0.29	1.42	8.0
13.67	5.5	52.8	1.53	1.37	6.7
21.33	5.5	52.2	2.31	1.35	6.1
40.50	5.4	51.7	3.31	1.14	5.6
63.50	5.3	49.4	4.98	0.99	4.8
81.67	5.3	50.0	5.58	0.88	1.8

Time (hr)	pH	Temp (°C)	H2SO4 5N (ml)	$[S(IV)]_t$ (M)	Glutaric (mM)
Run # G4 (0.1 mM Mn)					
0	5.5	53.9	0	0.88	9.2
0.50	5.5	61.7	1.15	0.73	7.3
1.00	5.5	66.1	2.73	0.58	5.9
1.50	5.5	66.7	3.97	0.41	4.4
2.00	5.5	65.0	4.66	0.33	3.3
2.50	5.5	62.2	5.33	0.29	3.1
3.00	5.5	60.0	5.66	0.24	2.4
3.75	5.5	58.9	6.07	0.19	1.6
Run # S 1					Succinic
0	4.5	48.0		1.00	9.5
0.33	4.5	55.1		0.83	8.4
0.67	4.5	62.2		0.67	8.1
1.00	4.5	64.4		0.53	7.4
1.33	4.5	66.4		0.36	6.9
1.67	4.5	67.8		0.19	6.9
2.00	4.5			0.06	5.8
Run # S 2 (1 mM Mn)					
0	4.4	44.4		1.02	9.3
0.33	4.5	55.6		0.91	8.4
0.67	4.5	63.3		0.69	8.8
1.00	4.5	68.3		0.44	9.2
1.33	4.5	71.7		0.18	9.2
1.67	4.0	71.1		0.02	9.8
1.92	2.9	65.0		-	8.9
Run # S 3 (1 mM Mn)					
0	5.5	53.0	0	1.33	6.3
0.50	5.5	60.5	1.38	1.12	6.6
1.00	5.5	63.2	4.29	0.92	6.8
1.50	5.5	64.5	5.35	0.77	6.9
2.00	5.5	65.6	8.02	0.59	6.7
2.50	5.5	68.0	10.56	0.34	6.3
3.00	5.2	72.2	11.62	0.05	6.0
3.50	4.4	61.5	11.62	0.01	5.9
Run # S 4 (0.33 mM Mn)					
0	4.5	40.0		0.87	8.4
0.33	4.5	51.5		0.72	9.5
0.67	4.5	58.5		0.56	10.2
1.00	4.4	62.0		0.44	10.3
1.50	4.4	6.50		0.25	10.2
2.00	4.4	68.0		0.03	10.0
Run # S 5 (0.1 mM Mn)					
0	4.4	46.5		1.01	8.7
0.50	4.4	56.0		0.81	6.1
1.00	4.5	64.0		0.48	4.9
1.50	4.4	6.82		0.22	4.7
1.75	4.3	71.0		0.06	4.6
2.00	2.5	66.0		-	4.5
Run # S 6 (0.2 mM)					
0	4.5	38.9	0	1.04	0.84
0.50	4.5	50.6	0.28	0.89	0.88
1.00	4.5	50.6	0.82	0.71	0.86
1.50	4.5	62.2	1.01	0.60	0.82
2.00	4.5	65.0	1.15	0.45	0.78
2.83	4.5	69.4	1.39	0.10	0.68

Time (hr)	pH	Temp (°C)	H2SO4 5N_(ml)	$[S(IV)]_t$ (M)	β-hydroxypropionic (mM)
Run # HP 1					
0	4.5	53.5	0	0.99	2.1
0.33	4.5	59.5	3.10	0.87	2.0
0.67	4.5	64.4	3.50	0.69	2.0
1.00	4.5	66.6	4.42	0.55	1.9
1.50	4.5	69.5	4.59	0.27	1.8
1.75	4.5	71.0	4.62	0.11	1.5
2.00	2.5	68.4	4.62	-	1.4
2.50	2.5	60.0	4.62	-	1.3
Run # HP 2					
0	4.5	48.9	0	0.93	11.8
0.50	4.5	59.7	2.74	0.74	10.5
1.00	4.5	64.4	2.74	0.49	10.4
1.50	4.4	67.8	2.74	0.25	10.2
1.75	4.3	68.9	2.74	0.12	10.2
Run # HP 3					
0	4.5	45.0		0.97	24.3
0.33	4.5	47.6		0.92	25.7
0.67	4.5	49.2		0.85	25.7
1.00	4.5	50.5		0.83	25.7
1.50	4.5	51.6		0.88	26.0
2.00	4.5	51.6		0.85	26.0
Run # HP 4 (1.0 mM Mn)					
0	5.5	52.0	0	0.83	25.9
0.33	5.5	57.5	0.89	0.70	22.6
0.67	5.5	64.2	4.82	0.55	22.1
1.00	5.5	70.0	8.05	0.29	22.3
1.42	5.0	72.0	8.58	0.03	22.0
Run # HP 5					
0	4.5	42.0	0	0.97	9.8
0.50	4.5	48.0	0.25	0.95	10.2
1.00	4.5	50.0	5.76	0.90	10.3
1.67	4.4	52.5	8.03	0.89	10.3
2.42	4.4	55.0	11.53	0.78	10.1
3.17	4.4	56.5		0.68	9.6
					Glycolic
Run # HA 1					
0	4.5	49.0		1.00	8.3
0.50	4.5	52.0		0.96	8.4
1.00	4.5	53.0		0.94	8.9
1.75	4.5	54.0		0.92	9.1
2.50	4.5	54.0		0.88	8.6
3.25	4.5	54.0		0.84	8.6
4.00	4.5	54.0		0.82	8.6
Run # HA 2 (1 mM Mn)					
0	5.5	43.0	0	0.80	9.9
0.33	5.5	50.0	0.31	0.74	10.3
0.67	5.5	55.0	0.48	0.64	10.1
1.00	5.5	59.0	0.48	0.55	10.8
1.33	5.4	65.0	0.85	0.30	10.6
1.67	5.1	70.0	1.11	0.07	10.7
Run # HA 3					
0	5.0	38.0		1.01	9.6
2.00	5.0	53.0		1.02	9.9
4.00	5.0	53.5		0.97	9.7
6.00	5.0	53.5		0.95	10.2
8.00	5.0	53.5		0.91	10.0

Time (hr)	pH	Temp (°C)	H2SO4 5N (ml)	$[S(IV)]_t$ (M)	β-hydroxypropionic (mM)
Run # HA 4 (0.1 mM Mn)					
0	5.0	45.0		0.94	10.1
1.00	5.0	52.5		0.89	9.8
2.00	5.0	54.0		0.84	9.9
2.50	5.0	55.0		0.80	10.0
3.50	5.0	55.5		0.75	9.5
4.50	5.0	55.5		0.69	9.9
Run # HA 5 (0.3 mM Mn)					
0	5.0	48.0	0	0.96	8.1
0.50	5.0	56.2	2.37	0.82	8.0
1.08	5.0	63.5	2.61	0.59	7.9
1.50	5.0	65.8	2.61	0.45	7.6
1.78	4.9	67.2	2.61	0.32	7.4

Time (hr)	pH	Temp (°C)	H2SO4 5N (ml)	$[S(IV)]_t$ (M)	Adipic (mM)	Glutaric (mM)	Succinic (mM)
Run # DBA 1 (1 mM Mn)							
0	5.5	49.4	0	1.36	1.1	5.2	0.6
0.50	5.5	46.7	0.21	1.22	1.0	5.1	0.8
1.00	5.5	60.0	0.48	1.10	1.0	5.0	0.9
1.50	5.5	60.6	0.73	1.00	1.0	4.9	1.1
2.00	5.5	61.0	1.09	0.85	1.0	5.0	1.4
2.50	5.5	61.1	1.32	0.75	0.9	4.6	1.5
3.50	5.5	67.8	2.14	0.42	0.8	4.2	2.0
4.67	4.9	64.4	2.73	-	0.6	3.2	2.8
Run # DBA 2 (1 mM sodium thiosulfate, 1 mM Mn)							
0	5.5	50.6	0	0.92	2.7	11.4	5.4
0.50	5.5	64.4	0.86	0.73	2.7	11.4	5.8
1.00	5.5	70.6	1.66	0.44	2.7	11.4	6.2
1.67	5.5	73.3	2.42	0.07	2.7	11.2	6.6
2.00	5.2	64.4	2.42	-	2.4	10.0	7.1
Run # DBA 3							
0	4.0	50.0	0	0.94	2.9	11.4	5.4
0.50	4.0	62.8	0	0.68	2.8	11.2	5.5
1.00	3.9	67.8	0	0.43	2.7	10.8	5.5
1.50	3.7	71.1	0	0.14	2.7	10.5	5.5
1.83	2.0	66.1	0	-	2.5	10.5	5.2
Run # DBA 4							
0	5.0	53.9	0	1.06	2.4	10.5	5.2
0.50	5.0	57.2	1.08	0.98	2.4	11.0	5.0
1.00	5.0	58.9	1.74	0.90	2.1	9.7	4.5
1.50	5.0	58.9	2.40	0.77	2.0	9.0	4.4
2.00	5.0	58.9	3.08	0.67	2.0	9.2	4.4
2.50	5.0	58.3	3.57	0.60	1.8	8.4	4.0
3.17	5.0	57.8	4.37	0.50	1.6	7.8	3.6
4.67	5.0	56.7	5.78	0.40	1.6	6.9	3.5
6.83	5.0	55.6	7.57	0.21	1.2	6.0	3.2
9.00	4.8	54.4	9.03	-	0.6	4.0	2.2

Time (min)	pH —	Temp (°C)	$[S(IV)]_t$ (M)	Malonic (mM)
Run # MA 1 (0.3 mM Mn)				
0	5.5	43.3	1.05	9.4
30	5.5	52.8	0.93	8.8
60	5.5	60.0	0.73	8.2
90	5.5	63.3	0.53	7.6
140	5.5	64.4	0.24	5.5
				Valeric(mM)
Run # V 1 (0.1 mM Mn)				
0	5.5	52.8	0.86	9.2
30	5.5	56.7	0.74	7.8
60	5.5	58.3	0.66	6.0
90	5.5	60.0	0.56	4.7
150	5.5	61.1	0.39	4.0
230	5.5	60.0	0.13	2.3
270	5.5	58.0	-	1.3

Time (min)	pH —	Temp (°C)	H2SO4 5N (ml)	$[S(IV)]_t$ (M)	Acetic (mM)
Run # AC 1 (1.0 mM Mn)					
0	5.5	119	0	1.42	10
30	5.5	136	0	1.24	9.8
60	5.5	142	0.46	1.08	9.0
90	5.5	143	0.79	0.97	8.5
120	5.5	144	1.17	0.84	8.0
210	5.5	157	3.21	0.16	7.0
240	4.0	156	3.39	-	5.7
					Fumaric(mM)
Run # F1 (1 mM Mn)					
0	5.5	51.0	0	1.43	6.8
0.50	5.5	58.8	1.77	1.11	5.6
1.08	5.5	61.9	3.01	0.98	4.1
1.50	5.5	63.0	3.61	0.91	3.0
2.00	5.5	63.9	4.20	0.78	2.4
3.00	5.5	65.8	5.04	0.47	1.5
4.00	4.4	68.0	5.31	0.02	1.8

Table XA.2 Detailed Data of Slurry Experiments in Closed System

Time (min.)	pH	Temp. (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Adipic (mM)
Run # NA1					
0	4.94	53.0	330	0.99	0.87
20	4.88	53.5	310	0.94	0.61
60	4.83	56.0	225	0.79	0.37
90	4.84	56.5	155	0.56	0.24
120	4.82	58.0	130	0.28	0.15
135	3.80	56.0	300	0.07	0.10
Run # NA2					
0	5.05	55.0	450	0.63	73
60	5.04	55.4	450	0.57	70
120	5.07	55.0	450	0.50	65
180	5.04	54.8	450	0.45	62
240	5.02	54.0	450	0.39	59
300	5.06	56.0	450	0.32	56
420	4.05	55.8	450	0.30	49
Run # NA3					
-	5.0	55	450	2.51	49
				2.06	24
				1.53	13
				0.78	4
				~0	2
Run # NA5, with 1 mM Mn, 1000 rpm					
0	5.00	52.5	90	0.84	10.89
20	5.01	60.0	165	0.47	10.43
40	5.05	62.0	90	0.16	9.52
54	4.79	60.0	475	0.03	8.67
final			4.75		8.53
Run # NA6, with 1 mM Mn, 800 rpm					
0	5.10	50.8	320	0.89	10.23
20	5.00	55.8	230	0.78	
40	5.04	55.8	250	0.66	10.12
60	5.01	55.6	275	0.52	
80	5.03	55.0	275	0.40	9.98
100	5.02	55.0	300	0.32	
120	5.00	55.0	275	0.17	9.43
150	4.90	56.0	320	0.05	8.55
155	4.62	55.0	425		
final			425		8.47
Run # NA7, 0.1 mM Mn					
0	5.09	53.8	320	0.73	11.5
30	5.05	58.0	95	0.48	9.2
45	4.99	57.0	95	0.41	8.9
60	4.98	56.0	30	0.27	7.1
70	5.00	55.5	30	0.15	6.1
85	4.77	54.2	230	-	5.3
Run #NA 8					
0				1.01	7.00
60				0.94	6.67
150				0.74	6.04
210				0.62	5.50
300				0.44	4.93
405				0.22	4.47

Time (min)	pH	Temp (°C)	Off Gas (mi/min)	$[S(IV)]_t$ (M)	Adipic (mM)
Run # NA 9 ([illegible] 10 mM, pH 5.5, 55°C)					
0				0.84	9.06
90				0.70	8.13
210				0.49	7.19
Run # NA 10 (1.0 mM KI, pH 5.0, 55°C)					
0				1.05	9.82
20				0.97	9.76
50				0.80	9.55
80	0.65	9.25			
125	0.45	9.09			
181	0.25	8.83			
					Glutaric
Run # NG1, 1 mM Mn					
0	5.00	55.0	520	1.05	10.5
15	4.94	54.5	445	1.00	10.5
35	4.92	55.0	420	0.95	10.2
60	4.90	55.8	400	0.83	10.0
90	4.90	55.2	435	0.75	9.6
121	4.90	55.6	370	0.60	9.6
155	4.89	54.8	300	0.29	9.1
Run # NG2, 0.03 mM Mn					
0	5.09	55.0	420	0.84	9.8
20	5.01	55.0	320	0.77	9.8
40	5.01	55.0	320	0.67	9.3
60	5.03	53.8	320	0.59	8.7
80	4.99	54.4	320	0.53	8.4
100	5.03	54.4	320	0.41	7.9
120	5.0	54.4	320	0.38	7.4
140	5.02	54.6	320	0.30	6.6
160	5.03	55.0	320	0.21	5.9
180	5.03	55.0	320	0.14	5.1
200	4.98	54.4	350	0.06	4.1
Run # NG3, 1.0 mM Fe					
0	5.04	55.0	420	0.82	9.8
20	4.96	56.2	270	0.74	9.6
40	5.08	55.5	270	0.62	8.6
60	5.06	55.5	275	0.50	7.9
80	5.02	55.0	295	0.39	6.7
100	5.02	55.4	305	0.32	6.1
119	4.96	55.2	320	0.24	5.5
140	5.07	55.0	330	0.17	4.9
160	5.03	55.0	330	0.14	4.3
Run # NG4					
0	5.12	53.8	410	0.86	3.7 3.00
30	5.01	55.8	375	0.73	4.0 2.70
60	5.01	54.8	330	0.57	4.1 2.13
90	5.03	55.6	320	0.33	4.0 1.67
Run # NG5					
0	5.06	54.0	420	0.83	4.5 0.97
20	4.98	54.0	320	0.76	4.3 0.95
40	4.96	54.0	305	0.70	4.3 0.91
60	4.97	54.0	310	0.63	4.3 0.84
80	4.98	54.0	275	0.53	4.2 0.75
100	5.00	55.0	230	0.40	3.9 0.58
120	5.04	56.0	165	0.19	3.7 0.32

Time (min)	pH	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	$[S(IV)]_d$ (mM)	Glutaric (mM)
Run # NG 7, 0.3 M NaCl						
0	5.04	58.0	360	0.58	8.87	0
15	4.99	55.2	265	0.48	8.74	0.18
30	5.00	56.2	250	0.33	8.42	0.68
45	5.01	57.0	240	0.17	7.73	1.43
52	4.98	56.8	265	0.11	7.58	1.89
Run # NG 8, 0.1 M NaCl						
0	5.00	57.0	320	0.54	10.0	0
15	5.01	55.4	330	0.45	9.30	0.44
30	5.01	55.0	330	0.35	8.32	1.19
45	5.01	55.2	330	0.26	7.35	2.10
60	4.99	56.2	330	0.16	5.83	3.15
75	4.98	55.8	360	0.08	5.79	4.58
90	4.67	52.6	475	0.06	5.79	5.58

Time (min)	pH	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Glutaric (mM)	Cumulative CO2(mM)
Run # NG 9, 0.03 M NaCl						
0	5.10	52.0	480	0.43	9.85	0
30	4.96	54.8	480	0.38	9.54	0.21
60	4.96	56.0	480	0.36	9.20	0.69
90	4.98	56.0	480	0.31	8.56	1.29
120	5.00	56.0	480	0.26	7.83	2.04
150	5.02	56.0	475	0.21	7.02	2.94
180	5.01	55.5	470	0.15	6.01	4.4
Run # NG 10						
0	5.07	55.0	400	0.50	9.95	0
30	5.01	54.0	435	0.38	9.84	0.17
60	4.99	56.0	435	0.32	9.43	0.47
90	5.02	55.0	435	0.26	8.81	0.84
120	5.01	55.0	435	0.21	8.26	1.26
140	5.02	55.0	435	0.17	8.21	1.61
Run # NG 11						
0	5.03	53.0	365	0.51	10.1	0
15	5.01	55.0	395	0.43	-	0.08
30	5.02	55.0	395	0.41	9.7	0.22
45	5.02	54.0	410	0.38	-	0.36
60	5.01	53.0	425	0.36	9.6	0.47
90	5.02	55.0	425	0.30	9.4	0.70
120	5.00	55.0	425	0.25	8.6	0.96
150	5.00	55.0	425	0.20	8.1	1.24
180	5.00	55.0	425	0.16	8.5	1.54
Run # NG 12, 0.03 mM Mn						
0	5.10	56.0	400	0.80	10.6	0
30	5.01	54.0	425	0.73	10.3	0.13
60	5.00	52.0	425	0.69	10.3	0.24
90	4.99	55.0	430	0.65	10.5	0.35
125	5.01	55.0	425	0.59	10.1	0.55
151	5.01	55.0	425	0.56	10.3	0.74
180	5.01	55.0	430	0.53	10.0	0.95

Time (min)	pH	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Glutaric (mM)	Cumulative CO2(mM)
Run # NG 13, 1 mM Mn						
0	5.10	54.0	390	0.91	12.0	0
30	4.99	57.0	340	0.73	11.8	0.11
60	5.00	55.6	305	0.56	11.0	0.32
75	5.00	55.2	305	0.45	10.1	0.47
90	5.01	55.0	295	0.36	9.3	0.66
105	5.00	55.0	295	0.21	8.6	0.89
Run # NG 14, 10 mM Mn						
0	5.06	54.0	360	0.65	9.5	0
20	4.98	56.0	340	0.54	9.4	0.04
45	4.96	55.0	320	0.38	9.2	0.14
60	4.97	54.2	320	0.29	9.2	0.20
80	4.96	55.0	320	0.18	9.0	0.29
Run # NG 15, 5 mM Mn						
0	5.15	51.0	470	0.91	10.3	0
15	5.02	56.0	320	0.83	10.4	0.11
30	5.02	55.2	320	0.73	10.3	0.34
45	5.02	56.0	320	0.61	10.1	0.61
60	5.02	57.0	320	0.52	10.1	0.88
75	5.02	55.5	320	0.40	9.9	1.11
90	5.01	54.0	320	0.29	9.7	1.32
105	4.99	55.0	320	0.18	9.4	1.49
Run # NG 16, 600 rpm						
0	5.20	52.0	450	0.58	10.5	0
80	5.00	55.2	450	0.54	10.3	0.09
140	5.00	55.4	450	0.52	10.2	0.18
200	5.00	55.5	450	0.45	9.9	0.31
280	5.01	54.8	450	0.42	9.6	0.50
360	5.01	54.8	450	0.36	9.4	0.75
420	5.00	54.8	450	0.32	9.1	0.99
Run # NG 17, 1000 rpm, 500 ml/min O_2						
0	5.07	50.0	500	1.16	11.0	0
60	4.99	54.6	490	1.13	10.2	0.16
120	5.00	54.5	480	1.09	9.7	0.36
195	5.01	56.2	470	0.97	9.3	0.74
240	5.01	55.0	480	0.94	8.7	1.00
360	4.98	54.0	470	0.78	8.4	-
Run # NG 19, 0.0018 mM Fe						
7	5.02	55.0	400	0.641	10.90	0.022
20*	5.00	55.6	420	0.614	11.11	0.146
70	55.2	5.00	420	0.515	10.89	0.622
92	5.00	55.0	430	0.467	10.01	0.889
116*	5.01	55.0	430	0.427	9.35	1.170
120	5.00	55.0	420	0.411	9.35	1.215
140	5.01	55.1	420	0.364	8.58	1.558
160	5.01	55.2	420	0.315	7.81	1.915
175	5.00	55.4	420	0.270	7.76	2.202
* additional 0.0018 mM Fe was added						
Run # NG 20, 0.009 mM Fe						
10	5.00	53.6	385	0.717	9.97	0.028
30	5.00	56.4	360	0.626	9.13	0.286
55	5.01	53.8	400	0.529	8.36	0.793
75*	5.01	55.4	415	0.469	7.59	1.170
93	5.00	53.0	370	0.418	6.85	1.501
120	4.99	55.0	370	0.293	5.50	2.738

Time (min)	pH	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Glutaric (mM)	Cumulative CO2(mM)
135	5.01	56.0	360	0.202	4.46	3.654
155	5.01	56.4	370	0.100	3.58	5.228
* 0.009 mM fe was added						
Run # NG 21, 0.054 mM Fe						
5	5.02	54.5	380	0.478	10.50	0.006
15	5.00	56.0	350	0.421	10.17	0.097
32	5.01	55.8	400	0.345	9.46	0.580
47	5.01	55.0	425	0.294	8.94	0.949
60	5.00	54.2	390	0.259	8.75	1.201
Run # NG 22						
10	5.00	53.6	460	1.070	10.91	0.006
40	4.98	55.4	460	1.050	10.73	0.034
70	4.98	55.2	450	1.013	10.82	0.072
100[a]	4.99	53.0	440	0.994	10.73	0.119
130	4.97	55.2	440	0.954	10.41	0.189
160[b]	4.97	55.8	440	0.896	10.04	0.308
190[c]	4.99	55.6	440	0.853	9.86	0.441
220	5.00	55.8	450	0.827	9.77	0.546
235	5.00	55.4	450	0.800	10.00	0.591
a. 0.1 mM NaNO3 was added						
b. 0.4 mM NaNO3 was added						
c. 0.5 mM NaNO3 was added						
Run # NG 23, 100 mM sodium nitrate						
5	5.07	54.0	445	0.796	8.42	0.002
30	5.00	55.0	445	0.747	8.09	0.073
60	5.01	55.6	445	0.711	7.54	0.235
90	5.02	54.0	340	0.634	7.44	0.425
100	5.01	54.0	330	0.574	7.15	0.497
121	5.00	56.0	275	0.429	6.71	0.711
135	4.99	57.0	250	0.312	5.97	0.901
153	4.98	57.0	250	0.175	5.89	1.203
Run # NG 24, 50 mM calcium nitrate,dissolved S(IV) = 1.2 mM						
5	5.01	54.8	300	0.521	9.41	0.005
75	5.01	54.6	300	0.489	9.08	0.140
151	4.99	54.5	295	0.464	8.80	0.275
225	5.00	54.8	295	0.436	8.47	0.396
300	5.00	54.6	295	0.417	7.89	0.520
390	5.00	54.8	295	0.384	7.26	0.669
Run # NG 25, 50 mM $Ca(NO_3)_2$, 1 mM Mn, $[S(IV)]_d$ = 2.8 mM						
10	5.03	54.0	285	0.615	8.69	0.013
30	5.00	55.2	255	0.522	8.31	0.069
55	5.01	56.2	240	0.373	8.20	0.304
82	5.02	56.2	220	0.199	7.21	0.748
Run # NG 26, 20 mM $Ca(NO_3)_2$, $[S(IV)]_d$ = 1.2 mM						
15	5.02	54.3	305	0.632	10.29	0.033
55	5.00	55.4	275	0.604	9.63	0.133
90	5.00	55.1	275	0.583	9.52	0.228
120	5.00	55.0	275	0.568	9.42	0.306
150	5.00	55.0	275	0.552	9.32	0.340
190	5.00	55.0	275	0.526	9.02	0.474
220	5.00	54.8	275	0.506	8.93	0.542

Time (min)	pH	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Glutaric (mM)	Cumulative CO2(mM)
Run # NG 27, 80 mM $Ca(NO_3)_2$, 1 mM $[S(IV)]_d$ = 0.9 mM						
5	5.03	55.0	350	0.740	10.40	0.005
30	5.02	56.5	310	0.621	9.90	0.012
50	5.00	56.2	285	0.494	9.16	0.364
70	5.01	56.6	265	0.332	8.47	0.766
90	5.01	55.0	255	0.146	7.59	1.273
Run # NG 28, 100 mM $Ca(NO_3)_2$, 1 mM Mn, $[S(IV)]_d$ = 1.0 mM						
10	5.00	54.0	425	0.993	10.01	0.019
35	4.99	55.4	400	0.912	9.79	0.103
65	5.00	55.4	380	0.808	9.24	0.304
95	5.01	56.4	350	0.665	8.42	0.653
120	5.00	56.8	300	0.500	7.48	1.151
150	5.01	56.0	300	0.233	6.16	2.233
160	5.01	57.0	310	0.094	5.78	2.938

Time (min)	Temp (°C)	pH	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Hydroxyacetic (mM)
Run # NHA 1					
0	52.0	5.05	470	0.75	10.0
10	55.0	5.01	470	0.75	10.0
120	55.2	5.01	475	0.75	10.0
205	55.2	5.01	470	0.75	10.0
340	55.0	5.01	465	0.75	10.0
Run # NHA 2 (0.1 mM Mn)					
5	54.8	5.01	420	0.72	10.8
30	57.0	5.01	400	0.64	10.4
50	55.5	5.02	375	0.55	10.2
70	54.6	5.01	345	0.45	9.5
90	56.0	5.02	280	0.29	8.4
Run # NHA 3 (11 mM Mn)					
0	54.8	5.08	460		
5	54.0	5.05	450	0.87	10.4
95	56.0	5.02	430	0.78	10.7
150	55.0	5.02	430	0.68	10.3
220	55.0	5.00	400	0.55	10.5
275	55.8	4.96	350	0.32	10.3
Run # NHA 4 (0.1 mM Mn)					
10	54.0	5.01	425	0.69	9.8
35	54.8	5.01	410	0.63	9.7
65	55.6	5.02	400	0.57	9.4
95	55.8	5.00	390	0.50	9.2
130	55.8	5.02	370	0.39	8.5
175	56.0	5.03	300	0.13	7.1
Run # NHA 5 (0.03 mM Mn)					
10	53.0	5.04	475	0.94	9.8
60	54.2	5.01	450	0.88	9.3
125	55.4	5.00	450	0.77	8.8
180	55.4	5.01	450	0.69	8.2
255	56.2	5.02	435	0.54	7.6
350	54.4	5.02	425	0.29	6.0
420	55.0	5.00	435	0.09	5.4

Time (min)	pH —	Temp (°C)	Off Gas (ml/min)	$[S(IV)]_t$ (M)	Formic (mM)
Run # NF 1 (1.0 mM Mn), 1000 rpm					
0	4.9	(55)	475	0.68	7.9
20	5.0		375	0.63	7.6
40	5.0		350	0.54	7.4
60	5.0		350	0.44	6.9
80	5.0		350	0.34	6.4
100	5.0		350	0.20	6.0
120	4.7		425	-	5.0
Run NF 2 (0.1 mM Mn), 1000 rpm					
0	5.0	52.0	475	0.67	8.3
30	5.0	52.2	445	0.64	8.1
60	5.0	53.0	430	0.61	7.6
75	5.0	54.0	430	0.59	7.5
Valeric (mM)					
Run # NV 1 (1.0 mM Mn), 1000 rpm					
0	5.0	55.0	475	0.52	7.4
20	4.8	55.0	210	0.27	7.2
40	4.8	56.0	210	0.10	7.1
60	3.5	54.0	475	-	7.0
90	3.5	55.0	475	-	6.8
Run # NV 2 (0.1 mM Mn), 1000 rpm					
0	5.0	53.0	475	0.67	7.8
20	5.0	56.0	285	0.58	7.3
40	5.0	58.5	250	0.43	6.4
60	5.1	56.5	210	0.26	5.8
80	5.0	55.0	195	0.07	5.0
					Ethyleneglycol(mM)
Run NEG 1					
0	5.05	55.0	475	1.48	2.24
80	5.00	55.4	450	1.45	2.17
380	5.00	55.4	450	1.25	1.79
Run NEG 2 (1 mM Mn)					
3	5.00	55.0		0.98	13.1
35	5.02	55.0		0.85	12.4
75	5.02	56.0		0.73	11.8
120	5.00	55.0		0.34	11.2

Table XA.3 Dissolved Sulfite Concentration Effect Studies by Continuously Feeding Calcium Sulfite Slurry

Time (min)	pH __	Temp (°C)	Off Gas (ml/min)	Sample (ml)	Glutaric (mM)	Succinic (mM)	CO2 (mM)
Run # NG 29 (Feedrate = 0.407 ml/min = 0.011 M/hr)							
0	5.00	53.0	320	5.0	10.20	-	-
47.5	5.01	56.2	310	6.0	10.07	0.35	0.40
97.5	5.01	56.0	305	8.0	9.40	0.368	0.83
142.5	5.01	56.0	305	6.0	9.08	0.92	1.21
182.5	5.00	56.0	305	10.0	8.72	1.16	1.54
227.5	5.01	56.0	305	10.0	8.50	1.43	1.93
287.5	5.02	55.8	305	8.0	8.42	1.60	2.43
Run # NG 30 (Feedrate = 2.0 ml/min = 0.179 M/hr)							
0	5.05	55.0	475	10.0	10.36	-	-
20	5.01	56.0	420	24.0	9.67	0.62	0.89
60	5.00	55.6	420	27.0	8.28	1.18	2.42
90	5.01	55.4	420	25.0	7.38	2.02	3.29
130	5.00	55.2	420	25.0	6.71	2.57	4.29
Run # NG 31 (Feedrate = 0.865 ml/hr = 0.088 M/hr)							
0	4.98	56.0	500	10.0	10.18	-	-
45	4.92	54.4	480	21.0	9.97	0.06	0.99
95	5.03	56.0	480	21.0	9.44	0.58	2.08
135	5.02	56.0	480	19.0	8.70	1.18	2.96
190	5.01	55.0	480	26.0	7.74	1.81	4.17
245	4.98	55.0	480	24.0	6.78	2.36	5.37
285	5.01	54.0	480	25.0	6.03	2.67	6.25
340	5.00	55.0	480	59.0	5.22	3.00	7.46
Run # NG 32 (Feedrate = 0.3351 ml/hr = 0.037 M/hr)							
0	5.00	55.0	475	0	10.0	-	-
15	5.01	55.5	460	12.0	9.93	0.06	0.15
65	5.00	55.2	450	19.0	9.25	0.03	0.69
110	5.02	55.0	450	46.0	8.59	0.10	1.17
170	5.01	55.0	450	20.0	7.82	0.11	1.81
210	5.01	55.5	450	17.0	7.31	0.13	2.23
260	5.00	55.0	450	48.0	6.76	0.18	2.76

Appendix B Instrumental Analysis

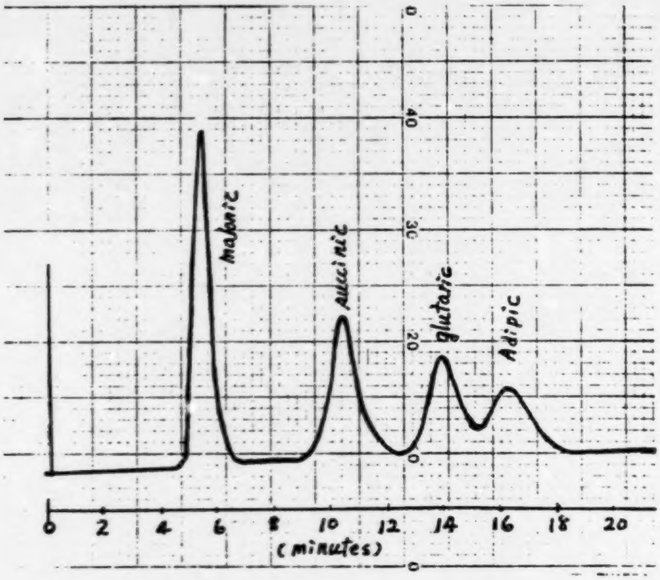

Figure XB.1 The Ion Chromatography Exclusion (ICE) Chromatogram

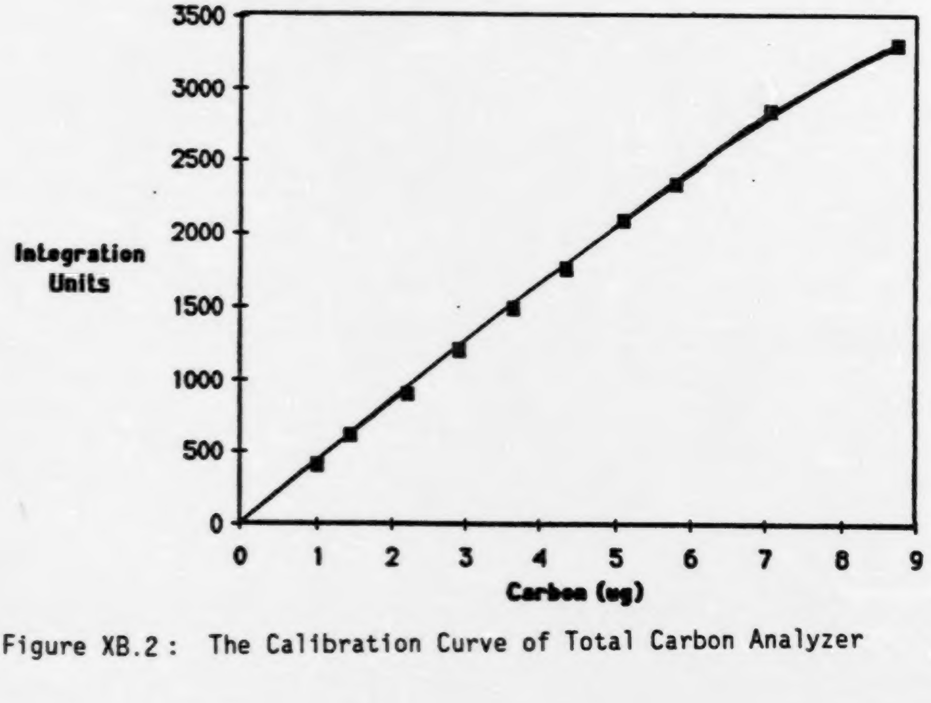

Figure XB.2 : The Calibration Curve of Total Carbon Analyzer

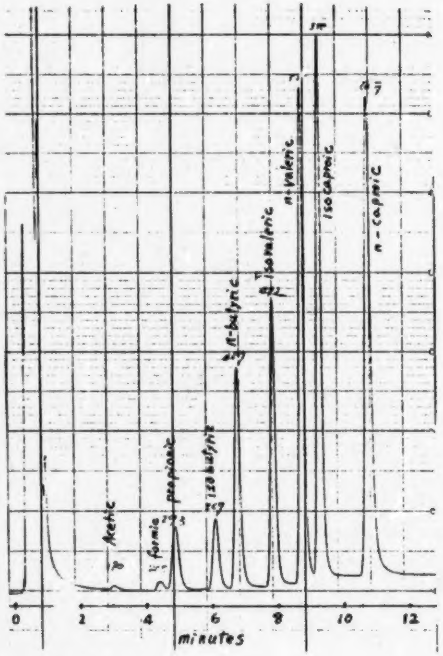

Figure XB.3: The GC Chromatogram of the Methyl Esters of Monocarboxylic Acids

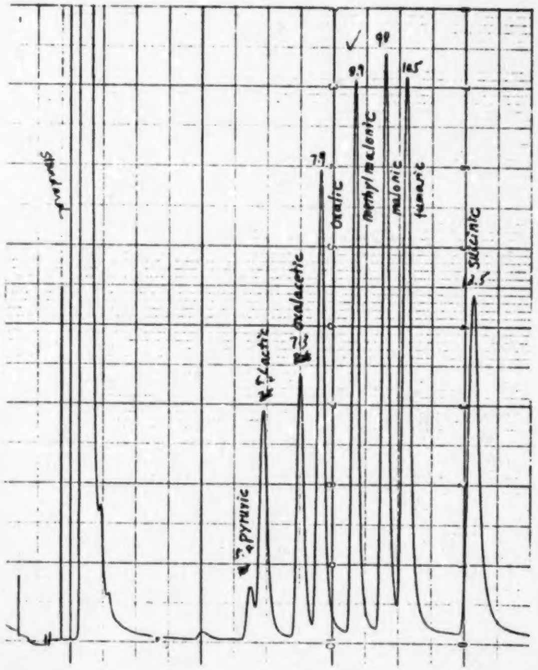

Figure XB.4: The GC Chromatogram of the Methyl Esters of Dicarboxylic Acids

Appendix C Identification of Glutaric semialdehyde

As shown in the GC chromatogram of Run A19 (pH 5.5, no Mn) (Figure XC.1), peaks 94 and 117 are the major liquid phase degradation products of adipic acid in the absence of manganese. The mass spectra of peaks 94 and 117 are given in Figures XC.2 and XC.3 respectively. Peak 94 is tentatively identified as the methyl ester of glutaric semialdehyde through the arguments presented in Figure XC.4 (fragmentation) and Table XC.1 (isotope abundance). Peak 117 is thought to be the acetal of glutaric semialdehyde, with a molecular weight of 176, because of the presence of m/e 145 (M - 31, or M - OCH_3) and the base peak at m/e 75. The most probable structure of base 75 is $[(CH_3O)_2\bullet CH]$, a fragment of the acetal $(CH_3O)_2CH(CH_2)_3CO(OCH_3)$, because of the resonance stabilization (McLafferty, 1980).

$$CH_3O\text{-}\overset{+}{C}H\text{-}OCH_3 \longleftrightarrow CH_3\overset{+}{O}{=}CH\text{-}OCH_3 \longleftrightarrow CH_3O\text{-}CH{=}\overset{+}{O}CH_3$$

Therefore, both peaks 94 and 117 could be derived from the same product, glutaric semialdehyde OHC-(CH2)3-CO2H. In ICE chromatogram, glutaric semialdehyde probably behaves as a strong acid and elutes with sulfate (Figure XC.5). The reaction of glutaric semialdehyde with bisulfite gives [HC(OH)(SO3)(CH2)3COOH]-, which can be converted back to glutaric semialdehyde by adding either acid or base (Solomons, 1978).

Glutaric semialdehyde is probably protected from oxidation in the presence of S(IV). In an experiment to test the oxidation of aldehydes in the presence of S(IV), slurry containing 1 M $CaSO_3$ solids, 1 mM formaldehyde, and 1 mM Mn was oxidized with oxygen at pH 5.0, 55 C. No formic acid was detected during sulfite oxidation, or at the moment when pH dropped because of the sulfite depletion. When pH was adjusted back to and maintained at 5.0 with sodium hydroxide solution after complete consumption of the calcium sulfite, formaldehyde was rapidly oxidized to formic acid. Manganese does not catalyze the oxidation of aldehyde in the presence of S(IV). Therefore, the formation of glutaric semialdehyde and glutaric acid must be via different pathways. Glutaric acid is not derived from the oxidation of glutaric semialdehyde in the presence of S(IV).

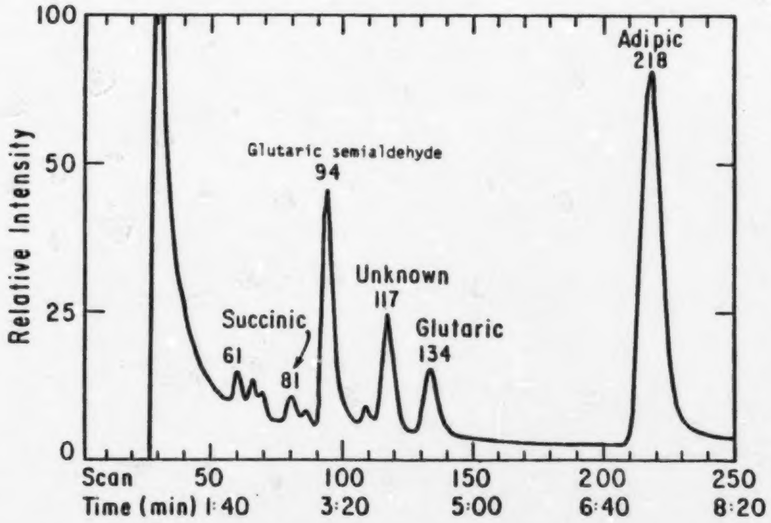

Figure XC.1 The Gas Chromatogram of the degradation products of A19

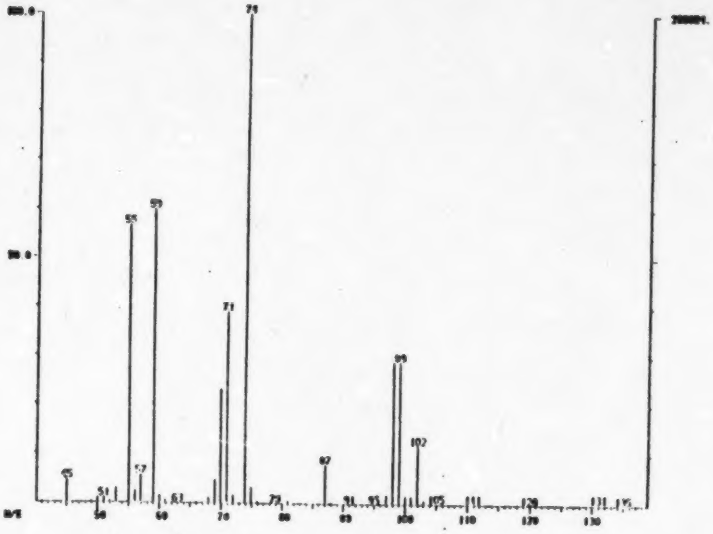

Figure XC.2 The Mass Spectrum of Peak 94 of A19

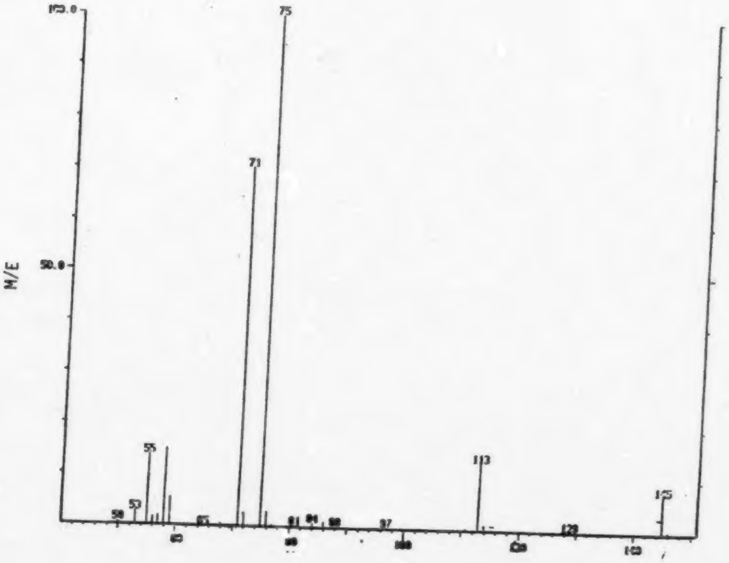

Figure XC.3 The Mass Spectrum of Peak 117 of A19

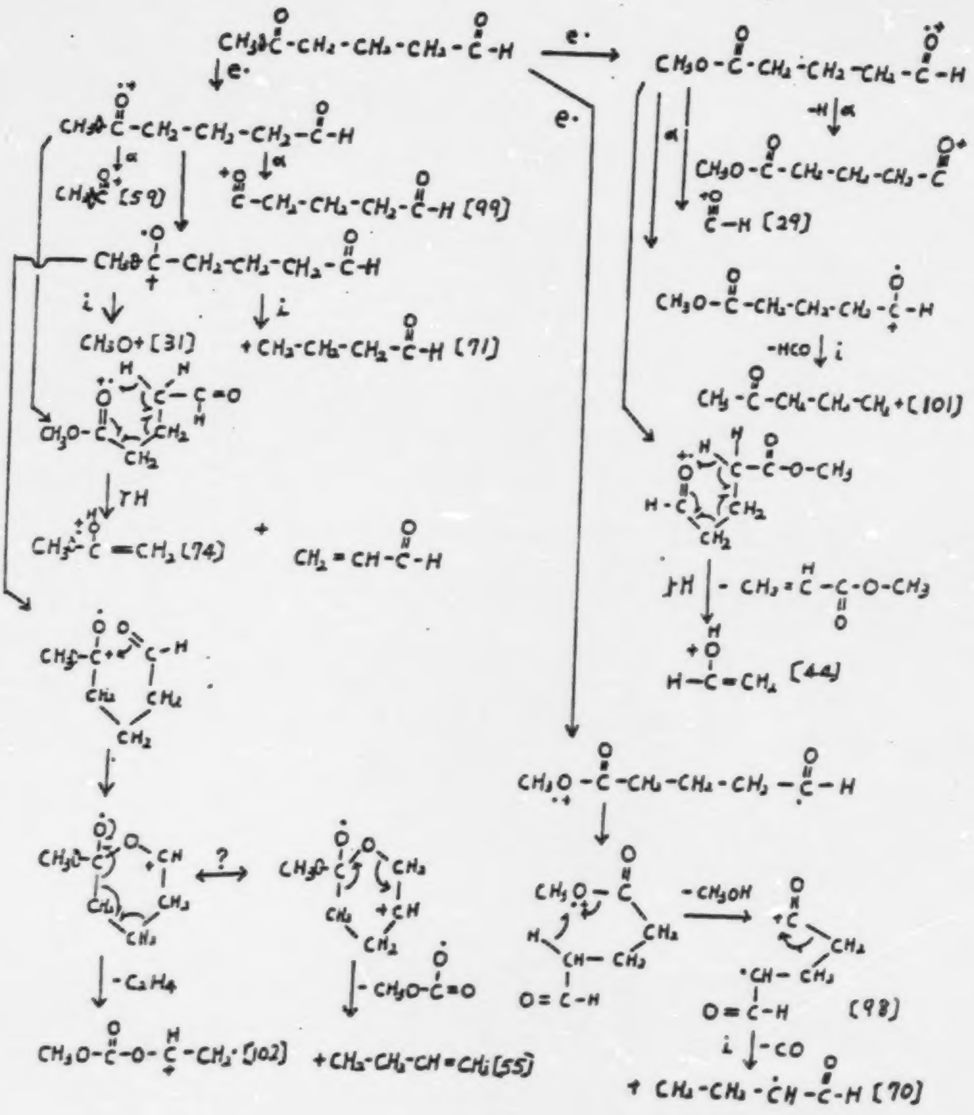

Figure XC.4 The Fragmentation mechanism of Methyl Ester of Glutaric Semialdehyde

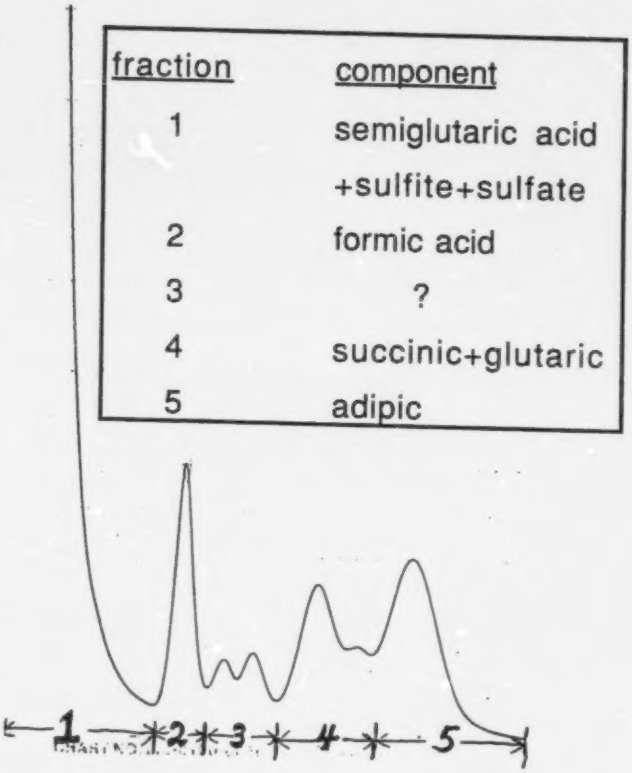

Figure XC.5 Ion Exclusion Chromatogram of Semiglutaric Aldehyde Containing Mixture

Table XC.1 Isotope Abundance and Formula of Fragments of Peak 94 in the GC/MS Chromatogram of A19

	P + 1 (%)		P + 2 (%)		
P(m/e)	measured	calculated	measured	calculated	Formula
55	4.36	4.43	--	0.08	C_4H_7
59	2.48	2.29	0.92	0.42	$C_2H_3O_2$
71	4.53	4.47	--	0.28	C_4H_7O
74	3.30	3.42	0.44	0.44	$C_3H_6O_2$
87	3.99	4.51	0.52	0.48	$C_4H_7O_2$
98	--	5.58	--	0.53	$C_5H_6O_2$
99	5.74	5.59	--	0.53	$C_5H_7O_2$
102	5.41	4.54	0.51	0.68	$C_4H_6O_3$

Appendix D Decarboxylation versus Degradation

A series of experiments were performed to correlate the relationship between glutaric acid degradation and CO_2 generation. In calcium sulfite slurry system, it was found that, in the presence of 0.03 mM Mn, up to 40% conversion, 1.3 moles of CO_2 were produced for every mole of degraded glutaric acid (Figure XD.1). It was also foud that, much more carbon dioxide was liberated for a conversion of 80% or higher (Table 5.5).

It has been observed that, in the oxygen oxidation of n-butylic and n-valeric acids labeled with ^{14}C in the carboxyl group, hydroxy- and keto-acids were not detected in the oxidation products, and the quantity of active CO_2 liberated corresponded to the quantity of acid oxidized , to within 2-3% (Denisov et al., 1977). However, it was also observed that CO_2 liberated was far beyond the quantity of acid oxidized when the reaction was carried out at 130-170°C in liquid phase (Agabekov and Mitskevich, 1968). Propably, the methylene groups are not as reactive as carboxyl groups but still competitive, especially when the concentration of carboxyl group drops down to an insignificant level.

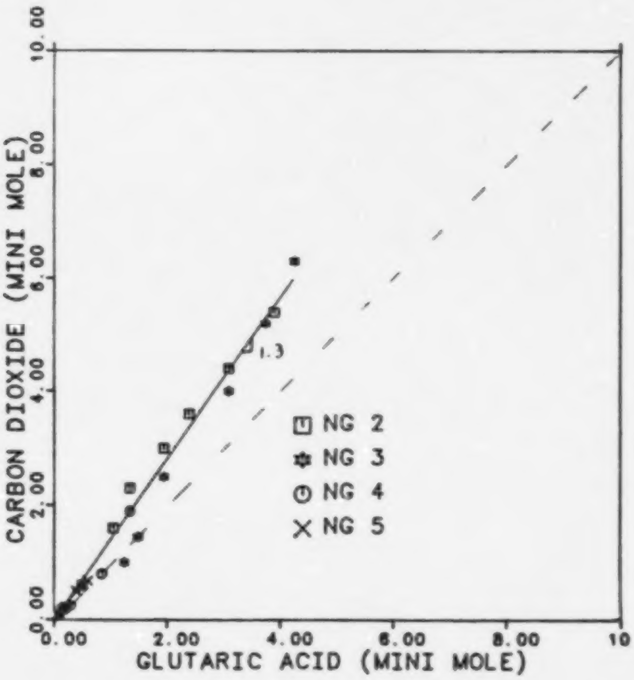

Figure XD.1: The Production of Carbon Dioxide from the Degradation of Glutaric Acid

Appendix E Derivation of the Oxidative Degradation Constant, k_{12} and Sulfite Oxidation Rate Expression

$$SO_4^- + OA^- \xrightarrow{kd1} SO_4^{2-} + OA$$

$$Mn^{3+} + OA^- \xrightarrow{kd2} SO_4^{2-} + OA$$

$$OA \xrightarrow{kd0} \text{Degradation}$$

$$Fe^{2+} + HSO_5^- \xrightarrow{ki1} Fe^{3+} + SO_4^-$$

$$Fe^{3+} + SO_3^{2-} \xrightarrow{ki2} Fe^{2+} + SO_3^-$$

$$Mn^{3+} + SO_3^{2+} \xrightarrow{ki2'} Mn^{2+} + SO_3^-$$

$$SO_4^- + SO_3^{2-} \xrightarrow{ki3} SO_4^{2-} + SO_3^-$$

$$SO_4^- + Fe^{2+} \xrightarrow{ki4} SO_4^{2-} + Fe^{3+}$$

$$SO_4^- + Mn^{2+} \xrightarrow{ki4'} SO_4^{2-} + Mn^{3+}$$

$$SO_3^- + O_2 \xrightarrow{kp1} SO_5^-$$

$$SO_5^- + SO_3^{2-} \xrightarrow{kp2} SO_3^- + HSO_5^-$$

$$SO_5^- + SO_3^{2-} \xrightarrow{kp2'} SO_4^{2-} + SO_4^-$$

$$HSO_5^- + SO_3^{2-} \xrightarrow{kp3} 2\ SO_4^{2-}$$

$$2\ SO_3^- \xrightarrow{kt} \text{stable products}$$

Assumptions:

1. steady state intermediates
2. Slow organic acid involved reactions comparing to their counterparts.

Let

$A_1 = k_{i1}[Fe^{2+}]$

$A_2 = k_{i2}[S(IV)]$

$A_2' = k_{i2}'[S(IV)]$

$A_3 = k_{i3}[S(IV)]$

$A_4 = k_{i4}[Fe^{2+}]$

$A_4' = k_{i4}'[Mn^{2+}]$

$B_1 = k_{p1}[O_2]$

$B_2 = k_{p2}[S(IV)]$

$B_2' = k_{p2}'[S(IV)]$

$B_3 = k_{p3}[S(IV)]$

The steady state equation for each intermediate:

Fe^{3+}

$$A_1[HSO_5^-] - A_2[Fe^{3+}] + A_4[SO_4^-] = 0 \quad \text{(eq. xf. 1)}$$

Mn^{3+}

$$A_4'[SO_4^-] - A_2'[Mn^{3+}] = 0 \quad \text{(eq. xf. 2)}$$

HSO_5^-

$$-A_1[HSO_5^-] + B_2[SO_5^-] - B_3[HSO_5^-] = 0 \quad \text{(eq. xf. 3)}$$

SO_5^-

$$B_1[SO_3^-] - B_2[SO_5^-] - B_2'[SO_5^-] \quad \text{(eq. xf. 4)}$$

SO_4^-

$$A_1[HSO_5^-] + B_2'[SO_5^-] - A_3[SO_4^-] - A_4[SO_4^-] - A_4'[SO_4^-] \quad \text{(eq. xf. 5)}$$

SO_3^-

$$A_2[Fe^{3+}] + A_3[SO_4^-] + A_2'[Mn^{3+}] - B_1[SO_3^-] + B_2[SO_5^-] - 2k_t[SO_3^-]^2 = 0$$

from eq. xf.4

$$[SO_5^-] = \frac{B_1}{B_2 + B_2'}[SO_3^-]$$

from eq. xf.1

$$[HSO_5^-] = \frac{B_2}{A_1 + B_3}[SO_5^-] = \frac{B_1 B_2}{(B_2+B_2')(A_1+B_3)}[SO_3^-]$$

from eq. xf.5

$$[SO_4^-] = \frac{A_1}{A_3 + A_4 + A_4'}[HSO_5^-] + \frac{B_2'}{A_3 + A_4 + A_4'}[SO_5^-]$$

$$= \left\{ \frac{A_1 B_1 B_2}{(A_3+A_4+A_4')(B_2+B_2')(A_1+B_3)} + \frac{B_1 B_2'}{(B_2+B_2')(A_3+A_4+A_4')} \right\} [SO_3^-]$$

from eq. xf.3

$$[Mn^{3+}] = \frac{A_4'}{A_2'}[SO_4^-]$$

$$= \frac{A_4'}{A_2'} \left\{ \frac{A_1 B_1 B_2}{(A_3+A_4+A_4')(B_2+B_2')(A_1+B_3)} + \frac{B_1 B_2'}{(B_2+B_2')(A_3+A_4+A_4')} \right\} [SO_3^-]$$

from eq. xf.6

$$\frac{A_1 B_1 B_2}{(B_2+B_2')(A_1+B_3)} + \frac{A_1 B_1 B_2}{(B_2+B_2')(A_1+B_3)} + \frac{B_1 B_2'}{(B_2+B_2')} - \frac{B_1 B_2 + B_1 B_2'}{(B_2+B_2')}$$

$$+ \frac{B_1 B_2}{B_2 + B_2'} - 2 k_t [SO_3^-] = 0$$

$$\therefore \quad [SO_3^-] = \frac{A_1 B_1 B_2}{k_t (B_2+B_2')(A_1+B_3)}$$

sulfite oxidation rate = $R_{ox} = 2 k_{p1} [O_2][SO_3^-] = 2 B_1 [SO_3^-]$

$$\therefore \quad R_{ox} = \frac{2 A_1 B_1^2 B_2}{k_t (B_2+B_2')(A_1+B_3)} = \frac{2}{k_t}\left(\frac{k_{p2}}{k_{p2}+k_{p2}'}\right) \frac{k_{i1}[Fe^{2+}] k_{p1}^2 [O_2]^2}{(k_{i1}[Fe^{2+}] + k_{p3}[S(IV)])}$$

$$k_{12} = \frac{\text{organic acid degradation rate}}{\text{sulfite oxidation rate}} \times \frac{\text{dissolved S(IV) conc.}}{\text{organic acid conc.}}$$

$$= \frac{(k_{d1}[SO_4^{=}] + k_{d2}[Mn^{3+}])[A^-][S(IV)]}{2k_{p1}[SO_3^{=}][O_2][A^-]}$$

$$= \frac{(k_{d1}[SO_4^{=}] + k_{d2}[Mn^{3+}])[S(IV)]}{2B_1[SO_3^{=}]}$$

$$= \frac{\left(k_{d1} + k_{d2}\frac{A_4'}{A_2'}\right)[SO_4^{=}][S(IV)]}{2B_1 \quad [SO_3^{=}]}$$

$$= \frac{\left(k_{d1} + k_{d2}\frac{k_{i4}'}{k_{i2}'}\frac{[Mn^{2+}]}{[S(IV)]}\right)[S(IV)]}{2}\left\{\frac{A_1B_2}{(A_3+A_4+A_4')(B_2+B_2')(A_1+B_3)} + \frac{B_2'}{(A_3+A_4+A_4')(B_2+B_2')}\right\}$$

$$= \frac{k_{d1}}{2k_{i3}}\left\{\left(\frac{k_{p2}'}{k_{p2}+k_{p2}'}\right) + \frac{\left(\frac{k_{p2}}{k_{p2}+k_{p2}'}\right)}{\left(1+\frac{k_{p3}}{k_{i1}}\frac{[S(IV)]}{[Fe^{2+}]}\right)}\right\}\frac{\left(1+\frac{k_{d2}}{k_{d1}}\frac{k_{i4}'}{k_{i2}'}\frac{[Mn^{2+}]}{[S(IV)]}\right)}{\left(1+\frac{k_{i4}'}{k_{i3}}\frac{[Mn^{2+}]}{[S(IV)]}+\frac{k_{i4}}{k_{i3}}\frac{[Fe^{2+}]}{[S(IV)]}\right)}$$

Appendix F Quality Assurance

This study was performed with a semibatch reactor system. The primary objective was to determine the effects of pH, S(IV), transition metal ions, halides, oxygen, and oxidation rate on the degradation of organic acids. The data collected were used to build up a kinetic model and provide clues for mechanism.

The final data were expressed in terms of k_d, and k_{12} for calcium sulfite slurry and sodium sulfite solution respectively. The concentrations of organic acid, total S(IV) were needed for k_d measurement.

Calcium Sulfite Slurry

Organic acid was analyzed by ICE after filtration and dilution (1:100) with distilled water. The major souce of error came from sample preparation (dilution). This measurement was with an error of 5%.

Total S(IV) was analyzed by iodometric titration. The uncertainty in the homogeneity of the sample results in a significant error. The characteristics of the calcium sulfite solids affect the homogeneity of slurry samples. Therefore, it is important to synthesize a calcium sulfite solid with enhancement of nucleation and with suppression of crystal growth to inhibit settling. Careful measurement could achieve a precision with 5% error.

k_d is obtained from the slope of log(organic) vs total S(IV). However, the slope is usually not a straight line, because of decreasing dissolved S(IV). The concentration of dissolved S(IV) varied from the saturated concentration (5 mM at pH 5.0) to almost zero. Therefore, the construction of the line is quite arbitrary, and results in about 30% uncertainty. Therefore, the k_d measurement has a confidence only within 40% error.

Sodium Sulfite Solution

Organic acid concentration was measured only for the initial concentration. Then the concentration was estimated from dilution caused by sampling and titration and from degradation reflected by CO_2 evolution. Because of low degradation, the precision is still high even with the relative high uncertainty of CO_2 evolution. The error was around 2%.

Iodometric titration was used for dissolved S(IV) measurement. Because of low concentration, microsyringe had to be applied to reduce volumetric error. The error was around 3%.

Oxidation rate was measured directly from the titration rate of sodium sulfite solution. Because of continual sampling, the oxidation rate is not on the basis of the same volume. However, the total amount of sodium sulfite added to the reactor can be fixed or easily measured. The error was still around 5%.

CO_2 evolution rate measurement should be divided into two parts: concentration and flow rate. The former might reach 10% error especially at low concentration; the latter has an error of around 5%. In total, CO_2 has an error of 15%. In conclusion, k_{12} measurement in sodium sulfite solution has an error of 25%, somewhat better than the k_d, measurement in calcium sulfite slurry, which has an error of 40%.

DISCLAIMER

QA/QC requirements are applicable to this project. The data contained in this report are NOT supported by QA/QC documentation as required by USEPA Quality Assurance policy.

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